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FILM FORMATION, FILM PROPERTIES, and FILM DETERIORATION

A Study by the
Research Committee of
the Federation of
Paint and Varnish
Production Clubs

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FILM FORMATION, FILM PROPERTIES, AND FILM DETERIORATION

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FILM FORMATION, FILM PROPERTIES, and FILM DETERIORATION

A Study by the Research Committee of the Federation of Paint and Varnish Production Clubs

CHARLES R. BRAGDON, *Technical Editor*

1958
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Foreword

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The technologists of the organic coatings industries believe that, in this book, they have made a positive contribution to the basic understanding of the phenomena which occur during the lifetime of a "paint" film. The scientists of our industry are well aware that a more fundamental understanding of the materials we use and the reactions we study is a requirement for the continuing creation of better coatings.

The search for knowledge is as old as man himself. In all generations, men interested in paints and varnishes have made contributions to this field and to these investigators of past and present we acknowledge our debt. As described at greater length in the Editor's Preface, this volume is an example of the service which is being rendered to the industry in our time by its technical organization, the Federation of Paint and Varnish Production Clubs. It typifies the gratifying results which are obtained when a group of energetic and dedicated people work together for the advancement of knowledge and the benefit of their Industry.

It is hoped that *Film Formation, Film Properties, and Film Deterioration* will prove helpful to those working in the research and development laboratories of the organic coatings industries and will, in addition, serve as a stimulus for further work of a basic nature in the years to come.

It is fitting that we pay tribute here to the scores of devoted individuals, the many constituent Clubs, and the various universities and commercial laboratories who contributed so effectively and so unselfishly to this long study. We particularly wish to thank Mr. Paul O. Blackmore who, as chairman of the Research Committee, was responsible for the initiation and prosecution of this project; Dr. J. S. Long who planned, inspired, and guided the original program; Dr. Walter O. Lundberg who faithfully served as project coordinator; and Mr. Charles R. Bragdon who skillfully edited and compiled the works of the various contributors into this volume. We feel confident that the Federation will grow and flourish as long as its members continue to give freely of their time and energies for such worthy educational and research activities.

MILTON A. GLASER
July 15, 1957 *President,* Federation of Paint and
Varnish Production Clubs

Editor's Preface

The Constitution of the Federation of Paint and Varnish Production Clubs sets forth that one of its main purposes is "to promote research and application of the sciences in the manufacture and use of . . . protective coatings, and to serve the welfare and interest of the public." This book is a compilation of widely dispersed but coordinated efforts aiming toward that goal.

Paint and varnish manufacturing in the United States and Canada is highly competitive. The industry numbers over 1500 concerns, some very small, some fairly large, but none controlling more than a few per cent of the total sales volume. This total, in 1956, was well over a billion and a half dollars, and the industry ranks third in U. S. consumption of chemicals, twenty-eighth in gross sales volume. The nature of the product and the variety of raw materials available are such as to permit wide variations of formula to meet varying requirements; a number of different combinations may lead to practically the same result. Even when paints and varnishes are bought on specification, as is the case with most government purchases and those of many large corporations, it is performance, not composition, that is usually specified. Every maker has complete leeway to choose his ingredients and to put them together as he feels will best meet any particular situation. Competition to improve quality is as strong as to lower the price.

Despite this intense competition, paint and varnish makers now show a marked spirit of cooperation in seeking ways to better their products; the jealous secrecy about formulas and processes prevalent up to the early 1900's has given way to a thirst for better understanding of fundamentals. The formation of local groups of technical and production men to gather and exchange non-competitive information began to be encouraged by executives, rather than frowned upon. By 1922 several such groups were ready to band together into a country-wide organization, the Federation mentioned in the first paragraph. John R. MacGregor of Eagle Picher Lead Co. had been a leader in starting several of the local clubs, and George B. Heckel, executive secretary of both the Paint Grinders' and the

PAUL OWEN BLACKMORE

was born in Toledo, Ohio, in 1903, and graduated from Cornell University in 1925. He spent four years with Grasselli Chemical Co. in Cleveland, then found his home in the paint, varnish and lacquer industry. After five years as technical supervisor of Mountain Varnish and Color Works and a year with Columbus Varnish Co., he joined the Finishes Division of Interchemical Corporation at Cincinnati as chief chemist. In 1943 he became director of its basic development laboratory, and in 1948 he moved with this laboratory to Newark, N. J. Since 1953 he has been sales promotion manager of the Division.

In Cincinnati, active in the local Production Club, he rose through its various offices to two terms as president (1938–40). In the Federation he advanced from assistant treasurer (1940–41), treasurer (1941–44), and vice-president (1944–45) to president (1945–46). A major contribution to the Federation was his successful campaign, while president, for admission of advertising to the *Official Digest.*

As chairman of the Federation Educational Committee (later renamed the Research Committee) from 1946 to 1954, he was in general charge of the research recorded in this book

National Varnish Manufacturers' Associations, was instrumental in organizing the Federation, of which he became the first secretary.

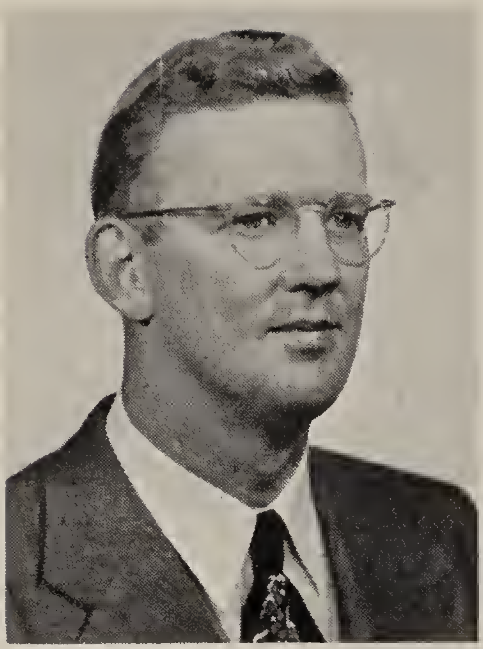
The Federation has grown steadily to an international membership, with 21 clubs in the United States, two in Canada, and one in Birmingham, England. All are healthy and enthusiastic; individual and firm membership numbers over 4000. The progressive ideas which are received and exchanged at the local monthly meetings and at the Federation's annual convention are recorded in the *Official Digest*, which it began to publish soon after its founding.

Each Club has a Technical Committee through which it conducts original studies and researches. Members volunteer their services and work actively on their own time or on time donated by their employers, on these projects. There is strong rivalry among the clubs to present at the annual convention, which is always well attended, the most worth-while report on work of this sort done during the year.

Besides these Club groups, the Federation has appointed from time to time a number of its own committees working to advance knowledge and proficiency in the operations of the industry. Important among these were the Scholarship Committee, charged with encouraging the establishment of researches on organic coatings in educational institutions, and its Technical Section, later called "Scholarship Technical Committee," which assisted in correlating researches carried on by the clubs themselves. All these activities have contributed to progress in paint technology, but up to the year 1946 none of them had gone very deeply into the fundamentals of paint behavior.

There had been a growing realization among members of the Federation that many of their research projects were mere gropings in a field where much deeper probing was necessary. At the same time, the work on these projects, and the organization of the Club Technical Committees which carried them out, provided a foundation for a more ambitious and fundamental program, one that would try to add materially to knowledge of the drying process and the subsequent behavior of films.

A program somewhat along this line had been discussed occasionally in meetings of the Federation Scholarship Committee. The idea finally crystallized early in 1946, when Paul O. Blackmore was president of the Federation, E. J. Cole chairman of its Scholarship



WALTER OSCAR LUNDBERG,

born in Minneapolis in 1910, studied at the University of Minnesota and at Johns Hopkins where a doctorate was earned in 1934. He taught next year at Hopkins. Returning to the University of Minnesota he engaged in research and attained professorial rank in 1944, the same year he became resident director at the university's Hormel Institute, of which he has been executive director since 1949. His fields of interest range from low-temperature calorimetry and electrode equilibria to antioxidants to fat metabolism and the organic, physical, and biological chemistry of fatty acids and their derivatives. He has published many scientific papers. As coordinator of the Film Research, he energetically followed up and harmonized the widely scattered projects and carried the program through to final success.

Committee, and Dr. James S. Long chairman of the Scholarship Technical Committee. Dr. Long (affectionately known as "Shorty" to his host of friends in the industry) drew up the main features of a coordinated campaign, which he presented at the February meeting of the Louisville Club (*Official Digest,* No. 255, 150 (1946)).

The chemical transformation on which the paint industry was founded and on which it still in great part depends—the drying of vegetable oils—has never been fully understood or explained. Worldwide research has produced considerable information and led to many theories, none of which completely fits and accounts for all the known facts.

The failure is due partly to the complexity of the subject and partly to the disconnected nature of the research studies. Linseed oil, the most widely used paint vehicle, is a mixture of glycerides of five or more fatty acids. Any one, two or three of these acids may be present in a given triglyceride molecule, so that the oil may contain a very large number of different compounds; no one has determined completely how many of the possibilities actually occur, or in what proportions. In addition, natural oils contain small amounts of a number of other compounds (antioxidants, wetting agents, etc.) which modify their behavior in ways that are not always understood.

Differences in the particular samples of any one oil (caused by soil characteristics, climate, and other factors) may have something to do with contradictory or irreconcilable results of different investigators. When so many constituents are present, it is hard to trace responsibility for a particular behavior to any specific one.

To simplify the problem, two expedients have been used. One method is to study compounds, such as olefins, of low molecular weight but with double-bond structures similar to those of drying oils. Some useful conclusions have been reached, although we cannot be sure that they apply with equal validity to the larger oil molecules. The other method is to work with pure fatty acid esters of monohydric alcohols, instead of trihydric glycerol. Here, in the absence of polymerization reactions, oxidation products can be separated and characterized, but that very absence robs them of value for the elucidation of the polymerization of drying oils.

In the plan presented to the Louisville Club in 1946 Dr. Long proposed a study of about two dozen pure compounds (oils and alkyd resins) of known composition, each containing only one of the more common unsaturated fatty acids found in natural oils. Paints made from portions of these pure vehicles, and the clear compounds themselves, were to be thoroughly investigated in film form. To spread the heavy load of a comprehensive research involving so many compositions, he proposed a simultaneous attack by different groups on separate phases (20 in all) of the general problem. Some of these studies could be handled by the Club Technical Committees; others required special equipment and services such as university laboratories could offer. He envisioned the gathering of the scattered but uniformly controlled data and fitting them together, as into a mosaic, to yield a well-rounded picture—a picture which would lessen the dependence of formulators on the method of trial and

JAMES SCOTT LONG,

born in York, Pennsylvania, in 1892, took degrees (Ch.E. and M.S.) at Lehigh in 1914 and 1915. While working up to professorship there (held from 1927 to 1934) he won a Ph.D. at Johns Hopkins in 1922. At Lehigh, from 1926 to 1934 he directed the research program on drying oils supported by Archer-Daniels-Midland Co., and he also served for 20 years as consulting chemist for Chester Enameling Co., where he made important improvements in patent leather finishes. In 1934 he became chemical director of Devoe & Raynolds Co., at Louisville, Ky., later a director of the company. He returned to academic pursuits as professor of chemical engineering at the University of Louisville in 1955.

Serving the Federation as chairman of the Scholarship Committee during 1945–46, he drew up the program for the Film Research Project, of which he acted as technical director until Dr. Lundberg's appointment as coordinator in June, 1949. Earlier in 1949 he represented the Federation, and presented papers, at the Rothesay meeting of the Oil and Colour Chemists' Association and at the meeting in Switzerland of the Federation of European Paint and Varnish Technical Societies. In 1953 he was the recipient of the George B. Heckel award. The next year he was chosen to give the Federation's Mattiello Lecture, and the Ohio section of the American Institute of Chemists awarded him its Gold Medal. He is a Fellow of the Royal Society of London and a member of many other scientific societies.

error, and enable them better to predict the influence on behavior of slight changes in a given component. Much of the work that was planned was, it was recognized, a retracing (under perhaps more closely controlled conditions) of studies already made; but this was necessary in order to obtain a complete, integrated picture of the physics, mathematics, and chemistry of film formation, film properties, and film deterioration.

The program was undertaken by the Federation as a major activity for the next seven or eight years. It was supervised at first by the Scholarship Technical Committee, under Dr. Long; but with changes in the Federation committee set-ups, it came under the Educational Committee and later under the Research Committee. As chairman of these committees, Paul O. Blackmore continued in general and fatherly charge from an administrative standpoint, and Dr. Walter O. Lundberg, Director of The Hormel Institute, University of Minnesota, was engaged to handle the maze of technical details and to direct the coordination between the various Production Clubs and the university and industrial laboratories.

Dr. Long presented a revised version of the project program in the *Official Digest* (No. 268, 262) of May, 1947. Other revisions were made, as circumstances indicated, after the experimental work had begun, either by the program coordinator or by the cooperators themselves.

The program contemplated three phases of activity: (*1*) preparation of the series (20 or more) of relatively pure drying compounds, (*2*) the carrying out of more than 20 closely related research projects on these compounds, and (*3*) a thorough study and integration of the data from all projects, followed by publication of results and conclusions. This book is the culmination of the third phase writes "Finis" for the time being to the Federation's effort in this area of endeavor.

It is felt that the program has focused attention upon several areas of potentially fruitful drying oil research and that this may inspire others to further exploration of these new avenues of approach.

The editor takes this occasion to acknowledge his indebtedness to those cooperators who have been helpful in clearing up doubtful points in the original reports, and especially to his wife, who was of invaluable assistance in all the stages of the editorial work.

October, 1957

Charles R. Bragdon
Technical Editor

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CHAPTER I

History of the Film Research

The compounds selected for the study of film formation, film properties, and film deterioration are not necessarily present in significant amounts in natural oils or commercial vehicles. They are all esters, or alkyd resins, of single fatty acids rather than of mixtures of these acids. However, collectively they include, or cut across, the more common types of unsaturated fatty acids of commercial oil vehicles. It was felt that the studies would bring out the differing influences on drying, weathering, etc., of the various fatty acids (and also of various polyhydric alcohols) in these vehicles—which, in Dr. Long's words, are sometimes "very bad mixtures." Most of the important contributions to our knowledge of oxidation and oxidative polymerization are found in a comparatively few papers based on studies of pure esters of single fatty acids.

The preparation of the compounds, several of which had never before been synthesized, required much preliminary work to develop suitable methods. It was begun in 1946 at the University of Minnesota under the direction of Professor George O. Burr, even before Dr. Long had presented his original program before the Louisville Club. But the first compound had not yet been made when Dr. Burr left the university to accept a research directorship in Hawaii. One of his former graduate students, Dr. Ralph T. Holman, also at the university, continued the work with the assistance of Mr. O. C. Elmer. Again, before they had completed the desired amounts of trilinolein, trilinolenin, and pentaerythrityl tetralinoleate, there was an interruption when Dr. Holman also left the university for a scholarship at the Nobel Medical Institute in Stockholm, Sweden. Mr. Elmer carried on, and arrangements were finally made with Dr. Walter O. Lundberg, director of The Hormel Institute of the University of Minnesota, at Austin, for preparation of the remaining 17 pure compounds by him, Dr. J. R. Chipault, and other Institute staff members. They also prepared a pentaerythritol ester of the mixed acids of linseed oil, primarily for use as a practice material, so that cooperators could familiarize themselves with the necessary techniques for their studies without wasting the more expensive pure compounds. In May, 1949, when the program began to need more attention than Dr. Long could give to it, Dr. Lundberg undertook the important assignment of coordinator of all projects. He accomplished an outstanding job in the face of many obstacles.

In addition to simple esters of oleic, linoleic, linolenic, and eleostearic acids with glycerol, pentaerythritol, and dipentaerythritol, the list of compounds included several long- and short-oil phthalic alkyds made with these acids and with glycerol and pentaerythritol. These are described and listed in detail in Chapter II. The quantities of each ranged from about 160 grams to more than 300.

Most of the projects were concerned primarily with films made from clear vehicles, but some of them also involved those made from pigmented compounds. The original intention was to pigment these with a specially purified grade of titanium dioxide, but with the realization that such a pigment would chalk excessively, the choice was a blend of 75% rutile titanium dioxide and 25% zinc oxide. Both these pigments were specially selected, and analyzed spectroscopically. D. W. Robertson and Hugh V. Allessandroni arranged for donation of the former by the Titanium Division of National Lead Company; American Zinc Sales Company gave the zinc oxide through the courtesy of L. P. Larson.

The operation of dispersing these pigments in the special vehicles was undertaken (1) by members of the Cincinnati-Dayton-Indianapolis-Columbus Club, under the supervision of Mr. Larson. In the laboratories of Battelle Memorial Institute, on a Saturday and Sunday (March 11 and 12, 1950), 13 men working on a well-organized assembly-line schedule incorporated the pigments, by milling on a 2 × 5-inch Fritzsche-Brown roller mill, in small amounts of each of the 20 pure compounds and 3 commercial vehicles, and sealed the resulting paints under nitrogen in approximately 200 glass tubes or ampules of appropriate sizes. Special precautions were taken to assure a 30% by volume ratio of pigment to vehicle solids, to avoid losses, and to minimize oxidation by air during the handling.

Driers

At an early stage in the program, P. M. Clark and John C. Bryan conducted experiments on several of the pure compounds to determine the optimum drier combination that would be reasonably effective with all. Their selection was 0.025% cobalt and 0.03% lead, both expressed as metal based on the weight of oil or alkyd solids. It was realized that this was low for the oleate esters and high for some of the linolenates, eleostearates, and alkyds, but it was felt that too many complications would be introduced by using a different dosage for each compound or group of compounds. The Nuodex Company, through the courtesy of Arthur Minich, specially prepared a solution of naphthenate drier containing, at 77° F., 2.5 mg. of cobalt and 3.0 mg. of lead (each as metal) per milliliter and supplied it in 2-ounce rubber-capped bottles ready for distribution, together with 1-ml. hypodermic syringes graduated in 0.01-ml. divisions so that measured amounts could be drawn off and added to the clear and pigmented vehicles.

Commercial Vehicles; Thinners

For comparison and control purposes in most of the projects, three commercial materials (a varnish grade linseed oil, a dehydrated castor oil, and a standard alkyd resin) were distributed with the pure compounds. They were supplied, together with a sufficient amount of mineral spirits, by Devoe and Raynolds Company through the courtesy of Dr. Long. For some of the special alkyds which were insoluble in mineral spirits, diisobutyl ketone was the solvent used.

Acknowledgments

The Henry A. Gardner Laboratory, Inc., of Bethesda, Maryland, loaned film applicators to a number of the cooperators. A great many other pieces of equipment and auxiliary materials were provided by various companies whose technical personnel participated in projects; in some cases, the time of these participants was also donated. Of course, much time was given by the individual members in each Production Club who supervised or actually performed work on the projects.

Experimental Work

The first experimental work began in 1948 at the University of Louisville, when only the first 3 compounds were ready. It was not until late in 1949, when all 20 of the special vehicles had been made, that most of the experimental work was taken up in earnest. Some projects were not begun until two years later, and a new one was added to the program even in the following year. After his appointment as coordinator in 1949, Dr. Lundberg visited all the cooperators, and made second and third trips where necessary to expedite the work.

Individual projects are described in detail in later chapters. The list which follows shows the number and name given each project in the revised plan, the group to which it was assigned, and the persons who were responsible for or carried out most of the work on each. The first person named in each group was in charge. It will be noted that in several cases where it was convenient or advantageous for two or more projects to be carried on simultaneously or in connection with each other, the same group undertook the additional ones

No.	Name	Cooperators
1.	Gain in Weight	National P. V. & L. Assn. Francis Scofield
	Gain in Weight (later transferred to)	University of Louisville* Dr. Gordon C. Williams C. I. Gandhi C. V. Metzler
2.	Ultimate Analysis	University of Louisville* Dr. Gordon C. Williams I. N. Cooperman M. M. Moudgill M. L. Johnson S. Y. Yuan
3.	Solvent Extraction	Same as 2*
4.	Distensibility and Tensile Strength	Philadelphia Club Dr. A. C. Elm New Jersey Zinc Co.
5.	Absorption of Organic Liquids	Same as 2*
6.	Spectrophotometric Studies a. Infrared	Pittsburgh Club R. W. Auxier and K. Adams Westinghouse Electric & Mfg. Co.

	C. E. Wilson Zimmerman Co.
b. Infrared	New England Club Westcott C. Kenyon J. J. Kirkland Selma Rossmassler Hercules Powder Co.
c. Ultraviolet	McGill University* Dr. R. V. V. Nicholls H. G. McAdie David Marshall W. H. Hoffman
7. X-Ray Studies	British Paint, Colour & Varnish Mfrs. Assn. Dr. Louis A. Jordan Dr. E. W. M. Fawcett
8. Exterior Exposure Tests	C.D.I.C. Club Lewis P. Larson Amer. Zinc Sales Co.
9. Water and Alkali Tests	Cleveland Club Dr. George Selden The Upco Co. R. C. Krueger The Arco Co.
10. Yellowing	Philadelphia Club Dr. E. B. FitzGerald R. A. Johnston E. I. du Pont de Nemours & Co., Inc.
11. Adhesion	New York Club Frederick M. Damitz National Varnished Products Corp. Fred S. Greenawald Nuodex Products Co.
12. Gloss and Gloss Retention	Same as *10*
13. Rate of Erosion	Southern Club* Dr. J. H. Coulliette Ewin B. Kiser, Jr. University of Chattanooga
14. Permeability	Baltimore Club* Dr. B. L. Harris Irvin Wolock A. Bialecki Johns Hopkins University

15. Structure of Pigmented Films	Unassigned
16. Molecular Size, Shape, and Weight	Louisville Club Dr. J. S. Long W. R. Lawton Devoe and Raynolds, Inc.
17. Chemical Analysis	Northwestern Club* Dr. R. E. Dunbar Robert J. Ludwigsen Wesley W. Page North Dakota Agricultural College
18. Depth of Oxygen Penetration	University of Michigan* Dr. L. L. Carrick W. J. Snoddon A. J. Permoda
19. Depth of Penetration of Water or Water Vapor	Same as *14**
20. Film Shrinkage	Same as *18**
21. Refractive Index	Same as *17**
22. Hardness and Abrasion Resistance	Same as *13**
23. Electrical Constants	Same as *11**
24. Oxidation Studies	University of Minnesota* Dr. W. O. Lundberg Dr. J. R. Chipault Evelyn McMeans E. C. Nickell

* Work supported in part by grant-in-aid from Federation.

In many cases where a project was not actually conducted by the Technical Committee chairman of the local Production Club, that officer or other club members helped ably in getting the work started and in keeping it moving. Especially was this true of the following:

R. C. Adams, Southern Club
J. C. Konen, Northwestern Club
R. W. Matlack, Philadelphia Club
Irving Pockel, New England Club
Howard G. Sholl, Baltimore Club
Carroll E. Wilson, Pittsburgh Club

Project 7, X-Ray Studies, was not established on a formal basis. Samples of trilinolein and trilinolenin were sent at his request to Dr. Jordan at the Paint Research Station at Teddington, England;

he had made a number of studies of films using x-ray techniques and offered to determine whether x-ray studies of films from these pure compounds would bring out characteristics of interest. He and Dr. Fawcett reported that, even when stretched 40%, or indeed up to 100%, in length, they failed to reveal any definite x-ray pattern. In other words, there was no systematic orientation of film structure. This project was therefore abandoned.

Project 15 was a very difficult one designed to determine the orientation of vehicle molecules on pigment particles, and the manner in which these particles arranged themselves from top to bottom of the film. It could have been carried out successfully only by personnel with highly specialized training and equipment, such as was available at only one location. Circumstances prevented the establishment of the project there, and since it was not essential to the integrity of the rest of the program, it too was abandoned.

Project 5, studies of the absorption of organic liquids by extracted films of the clear vehicles, failed from its beginning to yield any significant data; the techniques that were outlined for it proved unsuitable for measuring true absorptive properties. Since developing more adequate ones would probably have required more extensive research than was warranted, this project also ceased after the preliminary studies.

Projects 11 and 23, studies of adhesion and of certain electrical properties, were begun but never completed. Both depended upon success in laying, upon smooth metal panels, films of perfectly uniform thickness over their entire area. In spite of much hard work, technical difficulties proved insurmountable, and the project finally had to be given up.

With the exceptions described, all the projects listed above were completed. Number 24 was a new one, added after most of the others were well under way. It was intended to provide more detailed information concerning oxygen absorption, changes in ultraviolet absorption and in peroxide content, and other chemical measurements, to help in interpreting some of the data from other projects. Dr. Lundberg himself supervised it at The Hormel Institute.

The sponsors of this program knew at the start that it was a tremendous venture, but they did not realize quite how big a job it would turn out to be. The compounds chosen, although relatively close in composition to some of those present in natural oils, had many peculiarities; they were not easy to make, so that quantities were limited; and even though the cooperators sharpened their techniques of operation by careful practice beforehand with commercial materials, these peculiarities were not easy to control. The division of effort among so many working groups was another novelty which introduced further complications. But although some things were done which, in the light of afterthought, should have been done differently, most of the difficulties were successfully overcome, and the data produced were of great value.

Two difficulties proved particularly troublesome. One was the strongly reactive character of two of the special vehicles, trieleostearin and short-oil eleostearic glycerol alkyd. The triply conjugated unsaturation of the acid radical of these compounds and the absence of antioxidants triggered gelation in the ampules in which they had been sealed, either before or shortly after the vessel had been opened for addition of drier. A second batch of trieleostearin was made, treated with an antioxidant, and distributed to a few of the cooperators. A second batch of the other compound was also made, but no way was found to keep it from gelling before films were cast. Consequently we have only limited data for these two compounds.

The eleostearic compounds in general gave further trouble because of their tendency to dry to a dull, "frosted" film or one full of wrinkles. Readers unfamiliar with varnish-making technology may wonder why such misbehaving vehicles were included in the program at all. It was because tung oil, which contains 80% or more of eleostearic acid in ester form, was one of the most important oils for varnishes and enamels, with annual consumption of over 100,000,000 pounds. It, too, when used without modification, misbehaves in the same ways; but when carefully heat-treated (with considerable increase in viscosity), or properly blended by cooking or otherwise with 15% or more of a suitable resin, it produces stable vehicles that dry to smooth, glossy films, faster and harder and with better resistance to water, acids, and alkalis than those made from other natural oils. Comparisons of eleostearic esters and alkyds with those of oleic, linoleic, and linolenic acids were therefore highly desirable. But since all the Federation compounds were to be pure and essentially monomeric, no heat treatment or resin addition was permissible. Thus the eleostearates were handicapped in these comparisons, to an extent that was not foreseen.

The other serious difficulty was that with many of the pure compounds the wetting and spreading properties were very poor. Particularly on glass (even though it had been scrupulously cleaned), freshly applied films would "crawl" or draw together in droplets, leaving the glass apparently bare over considerable areas. Evidently a repellent monomolecular layer was formed on the glass, with a critical surface tension lower than that of the compound itself. The studies of Zisman and coworkers (2–8) have shown that such monolayers can be generated from a solution placed on a clean surface when saturated organic acids are present in concentrations as small as 0.001 mole per liter. Or they may result from instantaneous hydrolysis of pure esters *in situ* on the glass, catalyzed by the strongly adsorbed layer of moisture usually present on glass. The hydrolysis of the Federation compounds would have yielded in most cases relatively unsaturated acids, which tend to adsorb with the longest axis of the molecule in the plane of the solid surface so as to present essentially a moderately close-packed array of $—CH_2—$ groups uppermost, and with a critical surface tension of somewhat above 35 dynes per centimeter. Saturated acids, like stearic, orient themselves perpendicularly to the surface and present a close-packed array of methyl groups, with a critical surface tension of 22 to 25 dynes per centimeter and correspondingly greater repellency. Another possible mechanism, resulting in repellent surfaces, is adsorption of organic vapors present in drying ovens or in laboratory atmospheres.

Natural drying oils contain very small, but effective, amounts of surface-active agents which lower their surface tension and improve their wetting properties. The synthetic compounds contained none of these. Poor wetting properties would account also for imperfect adhesion, even though the crawling might be partially, or even to the eye completely, overcome by vigorous brushing or by rubbing with the finger tip at the time of application. Such expedients were employed by cooperators whose projects did not require absolutely uniform thickness of film; others apparently succeeded by pretreating the cleaned glass with a 5% alcoholic solution of benzoic acid.

Correlation and Evaluation

The final phase of the program was a study of the data and correlation and evaluation of the data to fit the scattered blocks into a complete mosaic. For this task the Federation secured the services of 18 carefully chosen and well-qualified people who gave their time and efforts, as an Evaluation Committee, to a correct interpretation of the experimental results. They were:

R. W. Auxier, Westinghouse Electric & Manufacturing Corp., East Pittsburgh, Pa.
L. J. Behan, St. Joseph Lead Co., Monaca, Pa.
I. M. Bernstein, Gotham Ink & Color Co., New York, N. Y.
D. S. Bolley, Baker Castor Oil Co., Bayonne, N. J.
R. E. Dunbar, North Dakota Agricultural College, Fargo, N. D.
E. B. FitzGerald, E. I. du Pont de Nemours & Co., Philadelphia, Pa.
B. L. Harris, Box 88, Route 1, Glen Arm, Md.
Paul Hess, Congoleum-Nairn, Inc., Kearny, N. J.
J. C. Konen, Archer-Daniels-Midland Co., Minneapolis, Minn.
L. P. Larson, American Zinc Sales Co., Columbus, Ohio.
J. S. Long, Devoe and Raynolds Co., Louisville, Ky.
W. O. Lundberg, Chairman, The Hormel Institute, Austin, Minn.
E. E. McSweeney, Battelle Memorial Institute, Columbus, Ohio.
H. F. Payne, American Cyanamid Co., New York, N. Y.
Francis Scofield, National Paint, Varnish & Lacquer Assn., Washington, D. C.
R. L. Terrill, Spencer Kellogg & Sons Inc., Buffalo, N. Y.
D. H. Wheeler, General Mills, Inc., Minneapolis, Minn.
G. C. Williams, University of Louisville, Louisville, Ky.

This committee held several meetings to plan evaluation procedures and discuss interpretations, and the members were thus enabled to work on the basis of standard criteria. Using a special data sheet, they first tabulated all usable data from all projects in suitable form for correlation; they applied methods of statistical analysis; and finally they compared the experimental results and drew up their interpretations and conclusions. For the statistical study, the committee's expert, Dr. E. B. FitzGerald of the Du Pont Company, gave many long hours of his own time to the tedious task of calculation. Using his results, supplemented by common-sense analysis of the data not susceptible to statistical treatment, the members of the committee then made their final reports.

Whereas this thorough study has probably brought out most of the relationships implicit in the scattered data, it has undoubtedly failed to discover all of them. Careful examination may be very resultful in unearthing further important information.

Published Reports

Progress reports were given at the Federation Conventions in 1946 (*Official Digest,* No. 263, 710), 1947 (No. 275, 659), 1948 (No. 287, 919), 1949 (No. 299, 864, 937), 1950 (No. 311, 1004), and 1951 (No. 323, 382). A number of reports on the preparation of the pure compounds and on the experimental work done with them were also published, making a total of 26 in all. They are listed below. Their substance and that of the hitherto unpublished reports, if not their complete detail, are contained in this book, with some corrections where errors have been discovered. All the originals of these reports, as well as copies of the many unpublished memoranda passing between cooperators and the program coordinator; are preserved in the office of the Federation in Philadelphia.

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Preparation of Linoleic and Linolenic Esters of Several Polyhydroxy Alcohols. Elmer, O. C., and R. T. Holman, *Offic. Dig.,* No. 263, 711 (1946).

Revised Outline of Federation Research Program. Long, J. S., *Offic. Dig.,* No. 268, 262 (1947).

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The Preparation of Alkyds and Additional Esters for Film Studies. Chipault, J. R., M. J. Hendrickson, and W. O. Lundberg, *Offic. Dig.,* No. 300, 53 (1950).

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Chemical Composition and Adsorptive Properties of Clear Films. Williams, G. C., *Offic. Dig.,* No. 311, 1020 (1950).

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Water and Alkali Tests. (Cleveland Club), *Offic. Dig.,* No. 311, 1042 (1950).

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CHAPTER II

Preparation of the Pure Compounds and Their Pigmentation

Twenty-three vehicles comprised the official roster of the program. Three of these were the commercial control materials, and 20 were the specially prepared single-acid esters and alkyds. The pentaerythritol ester of mixed linseed acids, supplied as a practice material as noted in Chapter I, and one or two other compounds were used in certain projects as main items; they were not, however, included in the regular list, shown below. The numbers in this list were assigned in the order of preparation of the pure materials, and the cooperators' tables of data usually followed the same order. However, in this book most data have been rearranged in the order of ascending functionality of alcohol and increasing unsaturation (or conjugation) of acid; this involves only moving pentaerythrityl linoleate and linolenate to their normal position between PE oleate and eleostearate. The control materials, Nos. 1, 2, and 3, will be found at the foot of most tables.

Precise chemical names, where unwieldy, were shortened from those given in parentheses below to the forms shown. Likewise, the frequently used abbreviations LO for long-oil and SO for short-oil were found handy for the alkyds; they, too, are employed throughout this book.

1. Varnish linseed oil
2. Dehydrated castor oil
3. Commercial alkyd
4. Trilinolein (glyceryl trilinoleate)
5. PE linoleate (pentaerythrityl tetralinoleate)
6. Trilinolenin (glyceryl trilinolenate)
7. Trieleostearin (glyceryl tri-alpha-eleostearate)
8. PE oleate (pentaerythrityl tetraoleate)
9. PE eleostearate (pentaerythrityl tetra-alpha-eleostearate)

10. DiPE oleate (dipentaerythrityl hexaoleate)
11. DiPE linoleate (dipentaerythrityl hexalinoleate)
12. DiPE linolenate (dipentaerythrityl hexalinolenate)
13. PE linolenate (pentaerythrityl tetralinolenate)
14. LO linoleic glycerol alkyd (MS)
15. LO linolenic glycerol alkyd (MS)
16. LO eleostearic glycerol alkyd (DK)
17. SO linoleic glycerol alkyd (DK)
18. SO linolenic glycerol alkyd (DK)
19. SO eleostearic glycerol alkyd (DK)
20. LO oleic PE alkyd (MS)
21. LO linoleic PE alkyd (MS)
22. LO linolenic PE alkyd (MS)
23. SO oleic PE alkyd (DK)

The simple esters, Nos. 4 to 13, were supplied as clear vehicles without solvent. The clear alkyds, 14 to 23, were 50% solutions either in mineral spirits (MS) or diisobutyl ketone (DK). All the pigmented compounds contained added mineral spirits.

Commercial Vehicles

Vehicles 1 to 3 were donated by Devoe and Raynolds Co. through the courtesy of Dr. Long. The first two came originally from their suppliers, and the third was of their manufacture. Their specifications follow.

Varnish Linseed Oil

Color, appearance, and odor, normal; specific gravity 15.5/15.5° C., 0.931–0.935; acid number (A.S.T.M. method), 1 maximum; iodine number (Wijs), 180 minimum; viscosity (Gardner-Holdt), A maximum; break test, clear and brilliant.

Dehydrated Castor Oil

Color, appearance, and odor, normal; specific gravity 15.5/15.5° C., 0.950–0.960; acid number, 2.0–8.0; viscosity (Gardner-Holdt), Z2–Z3.

Commercial Alkyd

Color, 7; wt. per gallon, 7.63 lb.; acid value, 5; viscosity, U;

glyceryl phthalate, 45.4%; oil (soybean), 52.3%; excess glycerol, 2.3%; solids, 50%; solvent, mineral spirits (95%), 50%.

The Special Vehicles

Mr. Elmer and Dr. Holman, who took over from Professor Burr and made about a pound each of Compounds 4, 5, and 6, described their procedures in the *Official Digest,* No. 263, 711 (December, 1946). The rest (7 to 23) were made at The Hormel Institute, and this work was reported by W. O. Lundberg and J. R. Chipault in the *Official Digest,* No. 288, 11 (January, 1949), and by J. R. Chipault, M. J. Hendrickson, and W. O. Lundberg in the *Official Digest,* No. 300, 53 (January, 1950). All the essential data in these reports are included in this chapter, for the benefit of others who may wish to repeat these preparations. Temperatures are Centigrade, and the petroleum ether used was of the low-boiling type.

Linoleic and Linolenic Acids

Armour and Co. kindly furnished some of their distilled linoleic acid; its iodine value was 148, tetrabromide number 33, peroxide value 4.7. It was brominated in chilled petroleum ether at —10°, the bromide recrystallized from ethylene dichloride, and debrominated by the procedure of Frankel and Brown (6). The resulting linoleic acid was not redistilled; it was almost colorless. (However, Elmer and Holman recommended direct quick saponification of corn oil in alcoholic KOH, and bromination of the mixed acids, as giving a higher yield.) The linolenic acid was prepared from linseed acids (donated by Archer-Daniels-Midland Co.) by brominating and debrominating, in ethyl ether. This acid had a slight yellowish tint but was not redistilled.

Esters

After considering and testing the various methods for preparation of triglycerides as proposed by (*a*) Wheeler, Riemenschneider, and Sando (11), (*b*) Daubert and Baldwin (3), (*c*) Black and Overley (1), and others, Elmer and Holman selected a modification of (*a*) as most satisfactory. A three-neck round-bottom pyrex flask (Fig. II-1) with ground joints (one for carbon dioxide intake, one for

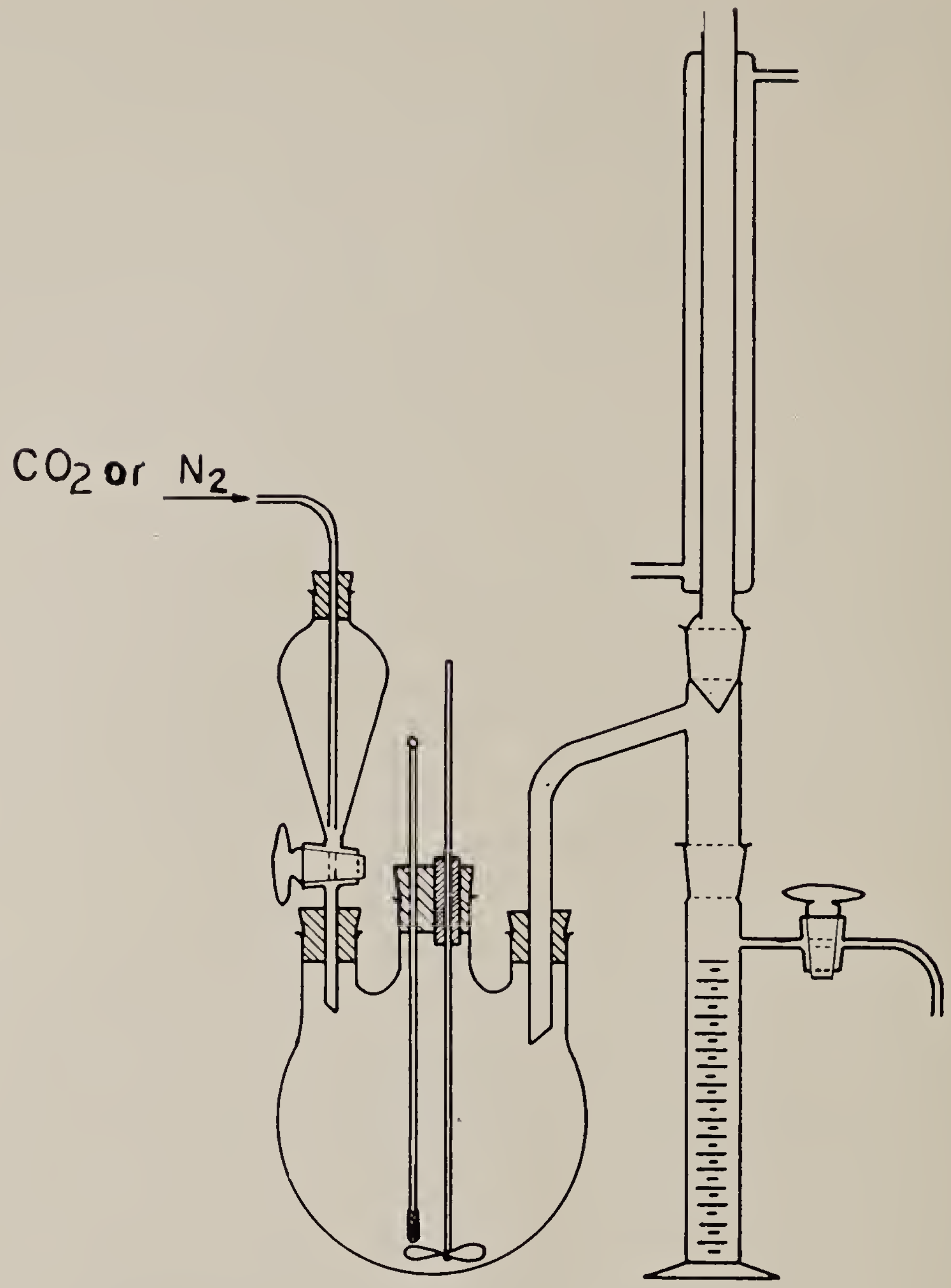

Fig. II-1. Apparatus for direct esterification.

thermometer, one for water-vapor removal) was used; mechanical stirring and double CO_2 intake were found unnecessary. Typical batches were made as follows.

Trilinolein (Glyceryl Trilinoleate), Compound No. 4

100 grams linoleic acid (0.357 mole), 10.8 grams glycerol C.P. (0.1175 mole), and 1.2 grams *p*-toluene sulfonic acid (as catalyst), were heated to 125° and held at this temperature for 6 hours while being agitated by a stream of CO_2. The cooled mixture was dissolved in 200 ml. petroleum ether and washed with 70% alcohol, containing 5% NaOH, until all acid was removed; one washing usually sufficed. The wash liquid was tested for alkalinity with phenolphthal-

ein. Five washings with 70% alcohol followed, and five washings with distilled water removed the dissolved alcohol. The petroleum ether solution was dried by standing over anhydrous sodium sulfate and the solvent was removed under suction on the hot water bath. The yield was 91 grams of ester (88.5% of theoretical); constants of this and of all the other pure compounds are shown in Table II-1. Recrystallization from acetone at —40° took out almost all the yellow color; the iodine value was raised to 171 (theoretical, 173.2).

PE Linoleate (Pentaerythrityl Tetralinoleate), Compound No. 5

100 grams linoleic acid (0.357 mole), 12 grams pentaerythritol (0.0883 mole; twice recrystallized), and 2 grams *p*-toluene sulfonic acid were reacted as in the procedure just described. Yields were low, averaging 85% of theoretical.

Trilinolenin (Glyceryl Trilinolenate), Compound No. 6

The same method was followed, using 200 grams linolenic acid (0.742 mole), 22.1 grams glycerol C.P. (0.24 mole), and 2.2 grams *p*-toluene sulfonic acid. The yield was 195 grams of an ester considerably darker than the trilinolein.

Other Esters

Dr. Long's first outline had suggested making esters from other polyhydric alcohols, such as dipentaerythritol, sorbitol, mannitol, and inositol. He had also mentioned the possibility of including esters of clupanodonic acid, which is found in some marine oils used as paint vehicles; but the program, even without these, was difficult enough to handle. Elmer and Holman, using the same catalytic method, obtained with dipentaerythritol and linoleic acid a poor yield of an ester with low iodine value. With inositol, again the yield was very low; the ester had low iodine value and high acid number, indicating very little reaction. They also used the oxalyl chloride (Daubert) method for one preparation of pentaerythrityl linoleate; it had a higher iodine number than from the catalytic method, and the UV absorption curve suggested the presence of conjugated trienes.

Since Elmer and Holman's method yielded poorly on dipentaerythrityl linoleate, and its long heating period at 125° might intro-

TABLE II-1
Properties of Clear Vehicles

Vehicle	Oil length	Solvent content	Iodine value		Saponification equivalent		Acid value	Hydroxyl value§	Specific gravity	Other
			Wijs	Theoretical	Observed	Theoretical				
Varnish linseed oil		0	180					0	0.9330 (15.5/15.5° C.)	n_D^{20}, 1.4786
Dehydrated castor oil		0					2.0–8.0	9.4	0.9550 (15.5/15.5° C.)	n_D^{20}, 1.4866
Commercial alkyd		50% MS						59.0		n_D^{20}, 1.4716
Trilinolein		0	170 (173*)	173.2	291.8	293.1	1.23	11.7	0.9257 (25/25° C.)	n_D^{20}, 1.4773 m.p., −11° C. Peroxide value, 0 Sulfur content, 0
Trilinolenin		0	253 (255*)	261.6	288.5	291.1	1.45	17.2		
Trieleostearin		0			288.9	291.1		13.7	0.9406 (25/25° C.)	n_D^{15}, 1.4848 Peroxide value, 0
PE oleate		0	83.8	85.1	294.4	298.5		8.0		
PE linoleate		0	165.4 (167*)	171.3	290.8	296.5	1.9	2.0	0.9332 (25/25° C.)	m.p., −245° C. Acetyl value, 0

PE linolenate		0	251.6	258.4	282.1 (?)	296.4		6.3	
PE eleostearate		0			288.9	291.1		13.9	
DiPE oleate		0	82.1	82.7	301.7	306.8		7.2	
DiPE linoleate		0	164.2	166.6	295.2	304.8		10.9	
DiPE linolenate		0	245.4	251.5	291.0	302.8		6.8	
LO linoleic glycerol alkyd	60.5	50% MS	98.0	103.9	171.4	161.5	9.6	34.4	
LO linolenic glycerol alkyd	60.3	50% MS	150.5	157.8	162.0	160.9	5.8	22.7	0.9100 (50% MS†) (25/25° C.)
LO eleostearic glycerol alkyd	60.3	50% DK			171.0	160.9	11.8	58.1	
SO linoleic glycerol alkyd	46.8	50% DK	76.0	80.7	150.8	139.4	6.1	53.1	
SO linolenic glycerol alkyd	46.5	50% DK	114.5	121.6	148.1	139.2	10.9	62.1	0.9570(50% DK‡) (25/25° C.)
SO eleostearic glycerol alkyd	46.5	50% DK			145.0	139.2	13.2		
LO oleic PE alkyd	75.1	50% MS	62.2	63.9	196.2	198.8	—	17.0	
LO linoleic PE alkyd	74.9	50% MS	126.8	128.4	195.9	197.8	—	18.0	
LO linolenic PE alkyd	74.8	50% MS	192.6	193.8	200.2	196.8	—	15.1	
SO oleic PE alkyd	46.2	50% DK	38.8	39.3	148.0	143.4	—	78.6	

* Values reported by Elmer and Holman, *Offic. Dig.*, No. 252, 711 (1946).

† Specific gravity of mineral spirits, 0.7786 (25/25° C.); calc. value of sp. gr. for compound free from mineral spirits is 1.0949.

‡ Specific gravity of diisobutyl ketone, 0.8073(25/25° C.); calc. value of sp. gr. for compound free from diisobutyl ketone is 1.1748.

§ Determined by method of Ogg, Porter, and Willits [*Ind. Eng. Chem., Anal. Ed.*, *17*, 394 (1945)].

duce unwanted isomerization and polymerization reactions, better methods were sought at The Hormel Institute for the other compounds, most of which were being made for the first time. That which Konen, Clocker, and Cox (7) employed in making trieleostearin by reacting methyl eleostearate with triacetin in the presence of sodium methoxide, had the advantages of relatively low-temperature operation and of rapid completion if the methyl acetate was removed as fast as it formed. In 30 minutes under a good vacuum the reaction was 90% complete without requiring a temperature over 100°. Eckey (5) described similar interchange reactions in triglyceride ester mixtures, reaching equilibrium conditions even below 49° with 0.1% or less of catalyst (sodium methoxide, sodium ethoxide, or other alkali metal alkoxides). This method was therefore used by the Hormel Institute team for making the remaining esters and some of the alkyds. They found that, for maximum yields under best conditions, all the reactants must be anhydrous and neutral; traces of water or free acid greatly reduce the activity of the sodium methoxide, which should be freshly made, finely divided, and highly dispersed. In all cases, elaborate precautions were taken, by use of vacuum or by blanketing with nitrogen which had been freed from oxygen by passing over hot copper, to protect from oxygen any materials subject to oxidation.

Sodium Methoxide Catalyst

Freshly cut sodium was dissolved in absolute methanol, excess of which was evaporated under vacuum. The white residue, finely ground in a mortar, was used at once. A more active catalyst would probably result if oxygen, as well as traces of water, were excluded during this preparation, or if Eckey's method (5) were followed.

Pentaerythrityl Tetraacetate

Technical monopentaerythritol (Heyden Chemical Co.) was refluxed with 10% excess of acetic anhydride for 2 hours, and the mixture was cooled, poured into water, and shaken vigorously. The crystals were filtered off, and washed by suspending in water and filtering, as many times as necessary to remove all free acid. The product was further purified in several stages by alternately dissolving in ethyl ether and precipitating with petroleum ether, until it had a sharp melting point between 80.7° and 81.0°. It then had a saponification equivalent of 76.03 (theoretical 76.04).

Dipentaerythrityl Hexaacetate

A similar method was followed except that dipentaerythritol was used and the refluxing was continued for several hours, and that when the mixture was poured into water the crude acetate separated as an oil. The water layer was decanted, and the oil was dissolved in ether and dried over sodium sulfate. Simultaneous cooling and strong agitation of the ether solution brought down crystals of the dipentaerythrityl acetate, which were filtered, washed with water, again dissolved in ether, and precipitated with petroleum ether. The latter procedure was repeated to yield a product which melted at 67.8° to 68.0° and whose saponification equivalent was 84.31 (theoretical 84.33).

Methyl Oleate

This was prepared from the methyl esters of olive oil fatty acids by the method of Wheeler and Riemenschneider (10). The methyl esters of fatty acids with less than 18 carbon atoms were removed by a preliminary partial distillation at low pressure in a Podbielniak Hypercal fractionating column with Heligrid packing and rated at 100 theoretical plates, and the residue was fractionated by several recrystallizations from acetone at —37° and —60°. After the final recrystallization, the methyl oleate was distilled through the fractionating column. Purities between 99.2 and 99.7% were indicated by analyses of several such preparations by the method of Brice *et al.* (2). A Beckman model DU instrument was used in the spectrophotometric analyses.

Methyl Linoleate

Methyl linoleate was prepared essentially according to McCutcheon (8). Tetrabromostearic acid was made from corn oil and recrystallized until a constant melting point of 115.5° was attained. It was then debrominated with zinc dust in methanol, and the product was esterified in the same solvent with 5 *N* hydrochloric acid. The ester was distilled through the Podbielniak column. Careful precautions against contact with oxygen were taken during and following the debromination step, and the final product was stored under oxygen-free nitrogen. The iodine value of several lots varied between 171.9 and 172.7 (theoretical 172.4). Spectroscopic examination of all samples revealed only slight traces of conjugated constituents.

The linoleic acid obtained in the debromination of tetrabromostearic acid is not identical with the original natural linoleic acid. The procedure converts small quantities of the starting material into some of the uncommon geometric isomers of that acid, which normally has the configuration of *cis*-9, *cis*-12, octadecanoic acid. However, the isomers are sufficiently small in amount, and probably similar enough to the natural acid in their drying mechanism, so that in the film studies they would be unlikely to have an appreciable effect on the behavior of the esters and alkyds made from them. The same comment applies to the linolenic compounds containing linolenic acid made in a similar way.

Methyl Linolenate

Raw linseed oil was the starting material for this similar preparation (8) of linolenic acid. The hexabromostearic acid was recrystallized several times from dioxane and ethylene dichloride to a constant melting point of 185.0°. It was debrominated in methyl alcohol with zinc dust in the absence of oxygen, and the acid esterified with methyl alcohol containing sulfuric acid. The ester, distilled through the Podbielniak column, varied in the iodine value of several lots between 259.0 and 261.4 (theoretical 260.4); the spectrophotometer showed no more than traces of conjugated constituents.

Methyl Eleostearate

First, a relatively pure alpha-eleostearic acid was made by saponifying tung oil and recrystallizing the fatty acids. They were dissolved in about twice their weight of methanol and kept under nitrogen at 4° for 48 hours. The crystals formed were filtered off and redissolved in methanol; crystallization was repeated twice. The melted fatty acids were then nearly water-white, and on spectrophotometric analysis conformed very closely with values reported by O'Connor *et al.* (9) for pure alpha-eleostearic acid. During all stages of this work, exposure to oxygen, to light, or to other agents that might catalyze conversion to beta-eleostearic acid was carefully avoided. The acid was then esterified by refluxing with 1.5 parts of methanol for several hours, using 3 to 4% of concentrated sulfuric acid as catalyst. The product was well washed with dilute sodium carbonate solution and the methyl esters were dissolved in a mixture of 320 ml. diethyl ether and 480 ml. methanol for each 100 grams. The crystals that formed on standing overnight at —45° were filtered off, and the residual solvent was evaporated under vacuum at 80 to 100°.

Fatty Acid Esters of the Polyhydric Alcohols

Figure II-2 is a diagram of the apparatus in which Compounds 7 to 13 and 20 to 22 were made. In the case of the esters, triacetin, or the acetate of pentaerythritol or dipentaerythritol, and a stoichiometric equivalent or a slight (1%) excess of the methyl ester of a fatty acid were weighed into flask *A*. In most lots, sodium methoxide amounting to about 0.5 to 1.0% of the total weight of reaction mixture was added; later studies indicated that with better precautions in its preparation and dispersion, less may be used. The flask was

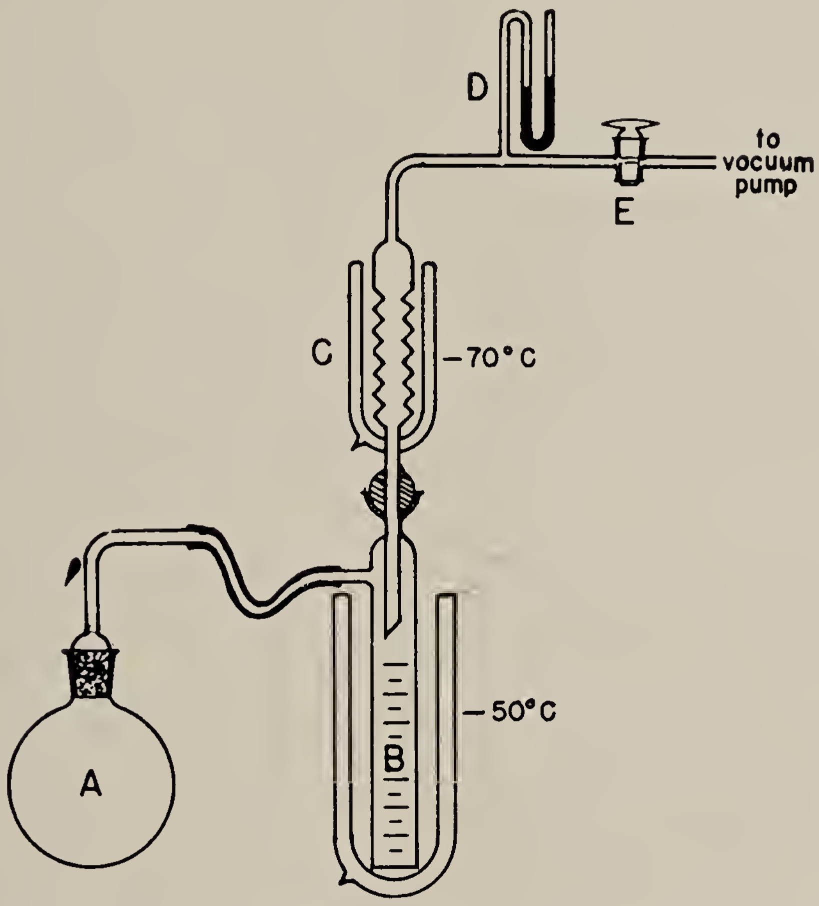

Fig. II-2. Apparatus for ester interchange reactions.

connected as shown and was evacuated as completely as possible with an efficient mechanical pump. The graduated receiver *B* was immersed in a mixture of dry ice and acetone (temperature about —50°) in a Dewar flask. The condenser *C* was cooled to about —70° by a similar mixture. Pressures were registered on manometer *D*.

The operator then closed stopcock *E*, immersed flask *A* in a water bath at about 60°, and raised the temperature slowly so that it neared the boiling point of water toward the end of the reaction.

The methyl acetate as it collected in *B* measured the progress of the reaction; at —50° its specific gravity is approximately unity, so that the reading in milliliters could be taken as the number of grams distilled over. In most of these compounds, the reaction yielded more than 90% of the theoretical amount after proceeding for about 30 minutes with frequent shaking of flask *A*. Occasionally stopcock *E* was momentarily opened to improve the vacuum.

When methyl acetate stopped coming over, purified nitrogen was admitted to bring the pressure back to atmospheric. The reaction mixture, dissolved in petroleum ether, was washed with 70% methyl alcohol to remove catalyst, any soap, and other impurities, and then with water. In order to assure complete removal of all traces of sodium, it was found desirable to precede the final washing with water by a single one with very dilute hydrochloric acid. The petroleum ether solution was dried over sodium sulfate and the solvent removed under vacuum.

Each compound was made in this manner in several lots of between 50 and 100 grams each, and the lots then combined to a final homogeneous batch of over 200 grams. This was divided into portions suitable for the use of cooperators and sealed in glass ampules under vacuum.

Typical examples of individual lots of each of these compounds follow:

Trieleostearin (Glyceryl Tri-alpha-eleostearate), Compound No. 7

226.04 grams methyl eleostearate, 56.22 grams triacetin, and a small amount of sodium methoxide catalyst were reacted as described above. However, in this case the catalyst was prepared according to Eckey's method (5), and 15 ml. of the suspension (1.38 *N*) in xylene was the amount originally added. At 50° to 60° the reaction went rapidly until two-thirds of the expected amount of methyl acetate was collected. From that point it slowed down, even at 80° to 90°, and 10 ml. more of sodium methoxide suspension had to be added to obtain satisfactory completion. The product, dissolved in 500 ml. of petroleum ether, was washed three times with 1-liter portions of 50% ethanol to remove catalyst and unreacted material, then dried, and the petroleum ether removed under vacuum. All operations involved in this and the making of the other eleostearic compounds were carried on under nitrogen and with no light except that from a photographic dark room lamp. The final product had the following spectral characteristics, which indicate that it contained no more than a few per cent of beta-eleostearic ester:

	Absorptivity	
Wavelength	Observed (in cyclohexane)	Calculated from O'Connor data (9)
269 mμ	146	143.1
271.5 mμ	161	161.1
276.5 mμ	119	117.3

PE Oleate (Pentaerythrityl Tetraoleate), Compound No. 8

15.4 grams pentaerythritol acetate, 61.0 grams methyl oleate, and 0.5 gram sodium methoxide were reacted in the manner described and 14.3 grams of methyl acetate were collected (theoretical 15 grams). Yield of pentaerythrityl oleate, 57 grams.

PE Eleostearate (Pentaerythrityl Tetraeleostearate), Compound No. 9

223.48 grams methyl eleostearate, 58.13 grams pentaerythrityl acetate, and 25 ml. of the sodium methoxide suspension in xylol reacted smoothly and virtually to completion at 60°. The reaction products were handled in the same manner as with trieleostearin, and yielded 182 grams of tetraeleostearate. Its absorption characteristics indicate that very little beta-eleostearate was present:

	Absorptivity	
Wavelength	Observed (in cyclohexane)	Calculated from O'Connor data (9)
269 mμ	144.5	141.5
271.5 mμ	163.0	159.2
276.5 mμ	119.5	115.9

DiPE Oleate (Dipentaerythrityl Hexaoleate), Compound No. 10

28 grams dipentaerythrityl acetate, 99.5 grams methyl oleate, and 1 gram sodium methoxide yielded 24.3 grams methyl acetate (theoretical 24.6 grams) and 98.0 grams of dipentaerythrityl oleate.

DiPE Linoleate (Dipentaerythrityl Hexalinoleate), Compound No. 11

28 grams dipentaerythrityl acetate, 100 grams methyl linoleate, and 1.2 grams sodium methoxide yielded 23.5 grams methyl acetate (theoretical 24.6 grams) and 98 grams dipentaerythrityl linoleate.

DiPE Linolenate (Dipentaerythrityl Hexalinolenate), Compound No. 12

20.1 grams dipentaerythrityl acetate, 69.8 grams methyl linolenate, and 0.5 gram sodium methoxide yielded 17.4 grams methyl acetate (theoretical 17.7 grams) and 70 grams dipentaerythrityl linolenate.

PE Linolenate (Pentaerythrityl Tetralinolenate), Compound No. 13

17.1 grams pentaerythrityl acetate, 66.3 grams methyl linolenate, 0.8 gram sodium methoxide were reacted until 16.2 grams of methyl acetate had collected (theoretical 16.5 grams). Yield of pentaerythrityl linolenate, 62 grams.

Long-Oil Glycerol Alkyds

In many attempts to make these alkyds by the double ester interchange method, the reaction always practically stopped at about 75% completion; the product was hard to wash and to free from catalyst. Therefore, the direct esterification method of Earhart and Rabin (4), with or without modification, replaced it. It was carried out in a three-neck round-bottom flask (Fig. II-1) with a separatory funnel having a nitrogen inlet in one side neck, a water-cooled Sterling-Bidwell type condenser in the other, a thermometer and a motor-driven stirrer in the center. Nitrogen was passed through at atmospheric pressure. Equimolar proportions of glycerol, phthalic anhydride, and fatty acid (plus a slight excess of glycerol) were employed.

Long-Oil Linoleic Glycerol Alkyd, Compound No. 14

61.6 grams phthalic anhydride (tech.), 40.5 grams redistilled glycerol (6.5% excess), and 7 ml. xylene were charged, and xylene was also added to the trap to the level of the side arm. Water began to come off at 160°, and this temperature was maintained until 3 ml. had collected. 116.1 grams linoleic acid was then added through the separatory funnel; the temperature was slowly raised to 250° and held there 2 hours. This rise of temperature was regulated by drawing off from the trap, below the condenser, xylene to a total amount of 14 ml.; 14.6 ml. of water collected in the trap (theoretical, 14.9 ml.). The final product (oil content 60.47%) was dissolved in mineral spirits to give a 50% solution.

Long-Oil Linolenic Glycerol Alkyd, Compound No. 15

Similarly, 61.4 grams phthalic anhydride, 40.0 grams redistilled glycerol (5% excess), and 7 ml. xylene were heated to 170°. Water began to evolve at this point. After 3 ml. came over, 115.4 grams linolenic acid was added, and by bleeding off 12 ml. of xylene the temperature of reaction was raised to 250°, where it was held 2.5 hours; 14.6 ml. of water was collected (theoretical 14.9 ml.). Oil content figures 60.30%. Again, a 50% solution was prepared by dissolving in mineral spirits.

Long-Oil Eleostearic Glycerol Alkyd, Compound No. 16

39.32 grams glycerol (3% excess), 61.38 grams phthalic anhydride, 115.39 grams eleostearic acid (prepared as previously described), and 200 grams tetralin (tetrahydronaphthalene) were heated together in the flask to 211° for 8 hours, during which time more than 95% of the theoretical quantity of water was evolved. After cooling, contents of the flask were poured into 2 liters of petroleum ether. The alkyd precipitated as a gummy resin, leaving the tetralin with the petroleum ether. After two additional washings with 1 liter each of petroleum ether, the last traces of volatile matter were removed by heating under vacuum, and the resin was dissolved in an equal weight of diisobutyl ketone (technical grade). Oil content of solids, 60.30%.

Short-Oil Glycerol Alkyds

The viscosity attained by these alkyds when made by the method of Earhart and Rabin using a small amount of xylene was so great at 75 to 80% of completion that they could not be stirred. By using higher proportions of higher boiling solvents (tetralin and diisobutyl ketone), by carefully controlling the rate of heating, and by gradually removing solvent to permit rise of temperature, gelation was avoided and the reaction brought close to completion. The same apparatus was used, and the molar ratio was 6 (plus slight excess) glycerol:7 phthalic anhydride:4 fatty acid.

Short-Oil Linoleic Glycerol Alkyd, Compound No. 17

82.5 grams phthalic anhydride, 46.0 grams glycerol (5% excess), and 200 grams of a 1:1 mixture of tetralin and diisobutyl ketone were heated until 3 ml. water collected at about 165°. 89.3 grams linoleic acid was added, and the temperature was raised to 190° to 195° for 3 hours, then slowly raised again to 250° and held 1 hour. Water collected was 14.8 ml. (theoretical 15.8). The remaining solvent was evaporated under vacuum on a hot water bath, and the resin dissolved in an equal weight of diisobutyl ketone. Oil content of solids, 46.79%.

Short-Oil Linolenic Glycerol Alkyd, Compound No. 18

82.8 grams phthalic anhydride, 46.0 grams glycerol (5% excess), and 200 grams of the same reaction solvent blend were held at 176° until 3 ml. water evolved; 88.9 grams linolenic acid were added, and the mixture was heated to 195° for 3 hours, then heated (slowly) to 250° and held an hour. 16.0 ml. water was collected (theoretical 15.8). Solvent was evaporated as before and resin dissolved in equal weight diisobutyl ketone. Oil content of solids, 46.45%.

Short-Oil Eleostearic Glycerol Alkyd, Compound No. 19

45.44 grams glycerol (3% excess), 82.78 grams phthalic anhydride, 88.92 grams eleostearic acid, and 200 grams tetralin were similarly reacted for 8 hours total, until a little over 90% of the theoretical quantity of water had been collected. The solvent was removed as from the long-oil eleostearic glycerol alkyd by pouring into petroleum ether and washing with additional portions of it, then evaporating under vacuum. Oil content of solids, 46.45%. The resin was redissolved in equal weight of diisobutyl ketone.

Pentaerythritol Alkyds

These could be made by the double ester interchange method if conditions were suitably selected. The molar ratios were in each case 1 pentaerythrityl tetraacetate : 1 dimethyl phthalate : 2 methyl ester of fatty acid for the long-oil compound.

Long-Oil Oleic Pentaerythritol Alkyd, Compound No. 20

24 grams pentaerythrityl tetraacetate, 46.7 grams methyl oleate containing 0.5 gram finely powdered sodium methoxide, were reacted under vacuum in the apparatus shown (Fig. II-2) on a hot water bath. Approximately 12 ml. of methyl acetate were collected, the loss of weight from the reaction mixture being the theoretical 11.5 grams. After cooling, 15.4 grams dimethyl phthalate containing 0.5 gram sodium methoxide were added, and heating was resumed until 11.0 grams reduction in weight (theoretical 11.5) occurred. The mixture, dissolved in petroleum ether, was washed with 70% ethanol until neutral, then with water. After drying over sodium sulfate, the solution was evaporated under vacuum. Oil content of resin, 75.06%. Four such lots of resin were combined and dissolved in an equal weight of mineral spirits.

Long-Oil Linoleic Pentaerythritol Alkyd, Compound No. 21

48.2 grams pentaerythrityl tetraacetate and 93.2 grams methyl linoleate containing 0.5 gram sodium methoxide were reacted as above; 22.2 grams methyl acetate came over (theoretical 23.5). 30.7 grams dimethyl phthalate with 2.0 grams sodium methoxide was introduced, and another 21.5 grams methyl acetate was collected (theoretical 23.5). The mixture, cooled, was dissolved in a 1:1 blend of ethyl ether and petroleum ether and washed with 70% alcohol until neutral, then with water, dried as before, and solvent removed under vacuum. Oil content of resin, 74.94%. Two batches thus made were combined and dissolved at 50% solids in mineral spirits.

Long-Oil Linolenic Pentaerythritol Alkyd, Compound No. 22

91 grams pentaerythrityl tetraacetate, 175 grams methyl linolenate, and 2 grams sodium methoxide, reacted as above, lost 45.7 grams (theoretical 44.3). With 58 grams methyl phthalate containing 4 grams sodium methoxide added, loss on further reacting was 38.5 grams (theoretical 44.3). One gram more of methoxide, to stimulate further combination, brought over 1 ml. more of methyl acetate. The product, dissolved in the same ether blend, washed with 80% alcohol and with water slightly acidified with hydrochloric acid, dried and solvent removed, was dissolved in an equal weight mineral spirits. Oil content of solids, 74.81%.

Short-Oil Oleic Pentaerythritol Alkyd, Compound No. 23

Failure greeted a number of attempts to use the ester interchange method, but direct esterification finally succeeded. Molar ratios were 4.5 pentaerythritol (+3% excess) : 7 phthalic anhydride : 4 oleic acid.

48.89 grams pentaerythritol, 87.54 grams oleic acid, and 200 grams tetralin were heated to reflux in the direct esterification apparatus (Fig. II-1) until virtually the theoretical amount of water was evolved. 80.33 grams phthalic anhydride were then added, and heating was continued at about 211° for 10 hours, until no more water came over. The product was washed with three 2-liter portions of 95% alcohol to remove almost all tetralin. Methanol was used for further washing and then the residual solvent removed by heating at 100° under vacuum for 4 hours. The hard brittle resin (oil content 46.24%) was dissolved in an equal weight of diisobutyl ketone.

The Pigmented Compounds

The titanium dioxide donated by Titanium Division, National Lead Co., was listed as Sample No. 288RM-2, with the following properties: oil absorption, 19.9; pH, 7.2; rutile content, 90%; and particle size distribution:

Above 1 micron	0.0%
0.75–1.0 micron	1.0
0.5–0.75 micron	6.0

0.4–0.5 micron	10.0
0.3–0.4 micron	21.0
0.2–0.3 micron	42.0
Below 0.2 micron	20.0

The spectrographic analysis was as follows:

SiO_2	0.10%	Mg	0.0005	W	0.01 −
Fe_2O_3	0.002	Cb	0.01 −	V	0.002 −
Al_2O_3	0.01	Cu	0.0004	Cr	0.002 −
Sb_2O_5	0.002 −	Pb	0.002 −	Ni	0.001 −
SnO_2	0.001 −	Mn	0.00005 −	Mo	0.002 −

The zinc oxide donated by American Zinc Sales Co. was of their acicular, lead-free Azo ZZZ-33 type, Sample No. J-9-122-9, with the following spectrographic and chemical analysis:

Ag	0.0009	Cu	0.001	Pb*	0.02
As*	0.003	Fe	0.001	Sb	Trace
Ba	N. D.	Ge	0.008	Si	0.26
Ca	0.0001	Mg	0.006	Sn	0.0001 −
Cd	0.13	Mn	0.0001 −	In	N. D.
Co	0.001 −	Ni	N. D.	Ga	0.002
Cr	N. D.				

The Federation Research Committee made the final decision (p. 2) to use these pigments in a 3:1 weight ratio and at a volume concentration of 30%, based on vehicle solids. The Columbus section of the C.D.I.C. Club's Technical Committee accepted the assignment to incorporate this mixture in the 23 vehicles, as well as to carry out Project 8, Outdoor Exposure Tests.

Early in 1950 Lewis P. Larson, Chairman, started to organize a rapid-fire production-line program for carrying out the pigmentation job. Many weeks were spent in planning and practicing the successive steps so as to speed them through with as little loss of time and material, as little exposure to air, and as great precision in attaining correct proportions as possible. Dr. E. E. McSweeney offered a constant-temperature room maintained at 78° F. and 50% relative humidity, as well as other facilities and services of personnel of Battelle Memorial Institute.

From 35 to 100 grams of each vehicle was supplied to the C.D.I.C. Committee from the precious stocks. Fourteen stations were assigned to individual cooperators in this program, which was enthusiastically carried out at the Institute on the weekend of March 11 and 12. It

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* Chemical assay.

TABLE II-2

Composition of Pigmented Compounds

Vehicle	Titanium dioxide	Zinc oxide	Total pigment	Vehicle solids	Solvent	Total vehicle
	Per Cent by Weight					
Varnish linseed oil	49.95	16.65	66.60	32.36	1.04	33.40
Dehydrated castor oil	43.18	14.39	57.58	28.64	13.78	42.42
Commercial alkyd	34.61	11.54	46.15	26.35	27.50	53.85
Trilinolein	44.28	14.76	59.04	28.60	12.36	40.96
Trilinolenin	45.50	15.17	60.67	29.39	9.94	39.33
Trieleostearin	42.95	14.32	57.27	27.73	15.00	42.73
PE oleate	42.40	14.13	56.53	27.39	16.08	43.47
PE linoleate	41.81	13.94	55.75	27.09	17.16	44.25
PE linolenate	42.62	14.21	56.83	27.52	15.65	43.17
PE eleostearate	42.13	14.04	56.17	27.21	16.62	43.83
DiPE oleate	40.94	13.65	54.59	26.44	18.97	45.41
DiPE linoleate	41.07	13.69	54.76	26.52	18.72	45.24
DiPE linolenate	43.86	14.63	58.49	28.35	13.16	41.51
LO linoleic glycerol alkyd	35.02	11.67	46.69	26.65	26.65	53.31
LO linolenic glycerol alkyd	35.02	11.67	46.69	26.65	26.65	53.31
LO eleostearic glycerol alkyd	33.58	11.20	44.78	27.61	27.61	55.22
SO linoleic glycerol alkyd	33.58	11.19	44.77	27.61	27.61	55.23
SO linolenic glycerol alkyd	33.58	11.19	44.78	27.61	27.61	55.22
SO eleostearic glycerol alkyd	26.29	8.76	35.05	21.61	43.34	64.95
LO oleic PE alkyd	35.02	11.67	46.69	26.65	26.65	53.31
LO linoleic PE alkyd	35.02	11.68	46.70	26.65	26.65	53.30
LO linolenic PE alkyd	35.02	11.67	46.69	26.65	26.65	53.31
SO oleic PE alkyd	33.58	11.19	44.77	27.62	27.62	55.23
	Per Cent by Volume					
Varnish linseed oil	23.37	5.85	29.22	68.16	2.62	70.78
Dehydrated castor oil	16.97	4.25	21.22	49.53	29.25	78.78
Commercial alkyd	11.80	2.96	14.76	34.43	50.81	85.24
Trilinolein	17.62	4.41	22.03	51.41	26.56	77.97
Trilinolenin	18.71	4.68	23.38	54.56	22.06	76.62
Trieleostearin	16.52	4.13	20.65	48.19	31.16	79.35
PE oleate	16.09	4.03	20.12	46.93	32.95	79.88
PE linoleate	15.66	3.92	19.58	45.69	34.72	80.42
PE linolenate	16.26	4.07	20.33	47.43	32.24	79.67
PE eleostearate	15.87	3.98	19.85	46.32	33.83	80.15
DiPE oleate	15.00	3.75	18.75	43.74	37.51	81.25
DiPE linoleate	15.09	3.77	18.86	44.01	37.13	81.14
DiPE linolenate	17.28	4.32	21.60	50.41	27.98	78.40
LO linoleic glycerol alkyd	12.08	3.02	15.10	35.25	49.65	84.90
LO linolenic glycerol alkyd	12.08	3.02	15.10	35.25	49.65	84.90

TABLE II-2 (*continued*)

Vehicle	Titanium dioxide	Zinc oxide	Total pigment	Vehicle solids	Solvent	Total vehicle
LO eleostearic glycerol alkyd	11.83	2.97	14.80	34.54	50.66	85.20
SO linoleic glycerol alkyd	11.84	2.96	14.80	34.54	50.66	85.20
SO linolenic glycerol alkyd	11.84	2.96	14.80	34.54	50.66	85.20
SO eleostearic glycerol alkyd	7.84	1.96	9.81	22.88	67.31	90.19
LO oleic PE alkyd	12.08	3.02	15.11	35.24	49.65	84.89
LO linoleic PE alkyd	12.08	3.02	15.10	35.24	49.65	84.90
LO linolenic PE alkyd	12.08	3.02	15.10	35.24	49.66	84.90
SO oleic PE alkyd	11.84	2.96	14.80	34.54	50.66	85.20

was a typical example of the precision planning and teamwork that went into this and other phases of the Federation research.

At various steps in the procedure, calculations had to be made to correct for small but unavoidable losses of vehicle and pigment in containers and on the three-roll mill, to compensate for the addition of solvents, and to determine various percentages, volumes, weights, and other necessary values before the paints could be finally sealed in the glass ampules. The containers in the process were frequently flushed with nitrogen, and the ampules were twice evacuated and filled with nitrogen before sealing.

In addition to Dr. Lundberg, who came from Austin to assist, and Messrs. Larson and McSweeney, those who participated in this operation or during other portions of the assignment were: Ed. J. Balkenhol, Benson G. Brand,* Marvin Coulter, R. Jack Deibert, Paul H. Dennison, Kenneth Jackson,* Wm. C. Kentner,* Donald Moseley, Ernest R. Mueller, Lou Nowacki, Chester Olson,* Arthur Sill, Richard Weirick, Victor Wernet, and Lou Wray.

The proportions of ingredients in all these pigmented coatings were carefully calculated both by weight and by volume and the figures are shown in Table II-2.

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CHAPTER III

Standard Conditions and Procedures

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With the purpose of assuring uniformity and comparability among the results obtained by cooperators, all of them adopted standard procedures and conditions in preparing and handling films, in so far as the nature of the project permitted. These procedures were described by the Research Committee or the Program Coordinator, in memoranda which were sent out at intervals to cooperators. In other respects, each group was encouraged to use its own initiative in conducting its studies and to keep in touch with the coordinator so that all the work would proceed harmoniously. Except as noted in the descriptions of individual projects, the conditions outlined in this chapter apply to all.

The limited supplies of special vehicles were allotted in small portions according to the probable needs for each project. These portions (sometimes as little as 3 or 5 grams) were sent out, together with more generous samples of the commercial materials and of drier and mineral spirits, to the cooperators as soon as they signified readiness to receive them. Pigmented compounds were distributed among five groups only. All were requested to store the materials in a cold dark place until they were ready to begin actual work, and to reseal them immediately under vacuum or nitrogen after taking out the quantities needed. Since the materials, in shipment, came in contact with the entire inner surface of the containers, these ampules were not themselves to be resealed; they were to be placed in test tubes which were to be drawn to a narrow opening, evacuated or well flushed with inert gas, then sealed, all with minimum subjection of the contents to heat.

Clark and Bryan in their drier tests (p. 3) found that driers did not reach full effectiveness until their mixture with the vehicles had stood for from 24 to 48 hours. It was therefore specified that the proper amount of drier should be added to freshly opened samples of the clear vehicles and the paints, the containers evacuated or flushed with nitrogen and again tightly closed, the contents well mixed, and the mixture held at 77° F. for 48 hours before any films were laid down. In some projects, films were laid without, as well as with, drier. In preparing the drier, the Nuodex Co. had made the following mixture:

41.67 grams Nuodex Cobalt 6%
12.05 grams Nuodex Lead 24%
Sufficient mineral spirits to make a total volume of 1 liter at 77° F.

Its content was therefore 2.5 mg. cobalt and 3.0 mg. lead per milliliter. When 0.1 ml. was added to each gram of nonvolatile vehicle, the final metal content in the film was thus 0.025% Co and 0.03% Pb per gram of solid compound, as required.

The standard wet film thickness chosen for clear films was 1.25 mils on the basis of 100% solids. The presence of 50% solvent in the alkyds made necessary a wet film thickness of 3.0 mils, to obtain 1.25 mils (approximate) thickness of vehicle solids. The low viscosity of the special oils made thinning unnecessary in most cases, but up to 5% of Eastman's very pure grade of toluene, 325-X, boiling between 110.2° and 110.4° C., was suggested for any necessary reduction.

Presence of 30% by volume of pigment in the special paints required a further thickness adjustment: a solvent-free film of 1.8 mils was calculated to provide the same 1.25 mil thickness of vehicle. Accordingly, the blade adjustment had to be set 0.55 mil greater than for the corresponding clear compounds with the same ratio of thinner to vehicle solids.

Choice of the substrate on which to lay the films was the subject of much discussion. Half-pint tin can lids, maple panels (for outdoor exposure), aluminum and other sheet metals were suggested at one time or another. The final selection for most projects (other than the spectrophotometric studies, or those where flat metal panels were required) was plate glass, to assure a perfectly flat, inert surface. Window glass or glass from photographic plates served where uniformity of film thickness was not critical. Glass free from contamination with oil or grease was recommended, and cleaning was to be done with a mixture of nitric and sulfuric acids, rather than with a dichromate–sulfuric acid mixture; it was feared that the chromic acid which might be tenaciously adsorbed on the glass might have a marked accelerating effect on oxidation. The cleaning was to be followed by thorough rinsing, and drying with a clean cloth; and in some cases also by additional treatment with a 5% benzoic acid solution in 95% alcohol (as mentioned in Chapter I) to minimize crawling.

Casting of the film was to be done preferably by means of a suitable blade; the Boston-Bradley blade, with appropriate shims, was first suggested, later the 6-inch Baker adjustable blade. Thickness of the drawn-down film was to be checked with the Interchemical wet film thickness gauge. The actual thickness might be found to be greater or less than the blade setting, depending on the viscosity of the vehicle; but it was noted that after a few trials with the commercial vehicles and the special practice compounds, and after visual observation of the approximate viscosity of the synthetic compounds, it was possible in most cases to adjust the blade setting so as to obtain very nearly the desired thickness on the first try. As a further check, it was suggested that film thickness be calculated from the weight and area of the film laid down, after removing nonuniform portions along the edges and making proper allowance for loss of solvent when present.

Both casting and drying of the films (except those to be baked) were to take place at 77° F. and 50% relative humidity, the latter condition especially emphasized as critical. Air was to circulate gently over the sample while drying. Illumination was to be provided by 40-watt General Electric daylight fluorescent lamps, so placed as to spread the light uniformly and at an intensity of 25 foot-candles at the surface of the sample. Except in cases where measurements were required during the drying period, films were to dry for one week before any measurements were made; however, the oleic acid compounds dried so slowly that measurements could be made only after some months, if at all.

Since it was anticipated that even with rigid adherence to these conditions, special factors might cause differences in drying rates at different locations, certain control measurements were recommended to be made by all cooperators as a check. These were (*a*) determination of "set-to-touch" time; (*b*) ultimate analysis of film for carbon, hydrogen, and oxygen after one week; and (*c*) determination of refractive index after one week.

Limitations of equipment and time prevented almost all groups from making any of these measurements except (*a*); however, for ease in determining the refractive index, a special technique was developed which is worth recording.

A strip of thin cellophane wetted on one side is placed wet side down on a sheet of glass with one end extending over the edge of the glass, and rolled into close contact free from wrinkles. Before the cellophane on drying has begun to curl, it is taped to the edges of the plate. After several hours for thorough drying, the assembly is ready for application of the film of vehicle, by a straight-edge applicator drawn in the usual manner toward the edge where the end of the cellophane laps over the edge of the glass. At desired intervals strips of film and cellophane approximately 1 × 2.5 cm. are cut out with a razor blade and applied face down on the polished prism surface in an Abbé refractometer. Air bubbles are squeezed out to assure intimate contact between film and prism, and the reading is made at 25° C.

With the Federation vehicles, different samples of the same material gave reproducible results only when they had the same film thickness and were dried under the same conditions; therefore the standard film thickness of 1.25 mils was recommended for all measurements. Following are readings obtained with the vehicles 1, 2, and 3:

Time	1. Linseed oil	2. Dehydrated castor oil	3. Commercial alkyd
0	1.4789	1.4870	1.4718
24 hr.	1.4920	1.4950	1.5260
48 hr.	1.4921	1.4951	1.5265
5 days	1.4929	1.4949	1.5270
9 days	1.4930	1.4953	1.5279

For these materials the index changed very little after the first day, so that it would not well serve in comparing changes due to aging in different laboratories. But it would indicate whether the same drying conditions had been in effect in different laboratories, if measurements were made in each at the end of one week.

CHAPTER IV

Gain in Weight, Ultimate Analysis, Solvent Resistance, Absorbency

Project 1 (Gain in Weight of Films on Drying) was designed to throw light on the mechanism behind the known fact that drying oils, when exposed to air, take up oxygen and gain weight, and on the relation between the composition of the oil and the amount and rate of gain. It was originally assigned to Francis Scofield at the laboratories in Washington of the National Paint, Varnish and Lacquer Association. His preliminary tests got under way very early; they included a number of exploratory variations of conditions which guided the choice of some of the standards of operation described in the preceding chapter. However, circumstances prevented his completing all the work required to establish proper correlation with other projects. This study was therefore transferred in December, 1951, to the Speed Scientific School of the University of Louisville, where Dr. Gordon C. Williams, Professor and Head of the Chemical Engineering Department, was already conducting three closely related investigations. On Project 1, two of his advanced students, Chandravadan I. Gandhi and C. Virgil Metzler, did the actual experimental work, which involved thousands of weighings and careful calculations.

Gain in Weight, Project 1—Washington Series

Both in Washington and Louisville the films were laid on glass photographic plates that, after complete removal of the emulsion, had been thoroughly cleaned. Scofield weighed his samples by difference from a small bottle containing a short-stemmed artist's brush, with which the material was spread uniformly over the area. For a 3 × 4-inch plate he used about 287 mg. of sample containing the prescribed amount of drier, equivalent to about 262 mg. non-volatile oil, and laying a film of about 1 mil dry thickness. His drying conditions were: temperature 25° ± 0.5° C., relative humidity 50 ± 5%, light intensity (from fluorescent ceiling lamps) 15 foot-candles. A turntable placed behind an electric fan and rotated by a motor at 2 r.p.m. assured even circulation of air over the plates placed on it.

Influence of Variables

In Scofield's report (2) he covered much of the preliminary work aimed at determining optimum conditions for the experimental procedures. Figure IV-1 shows a typical run on a linseed oil film

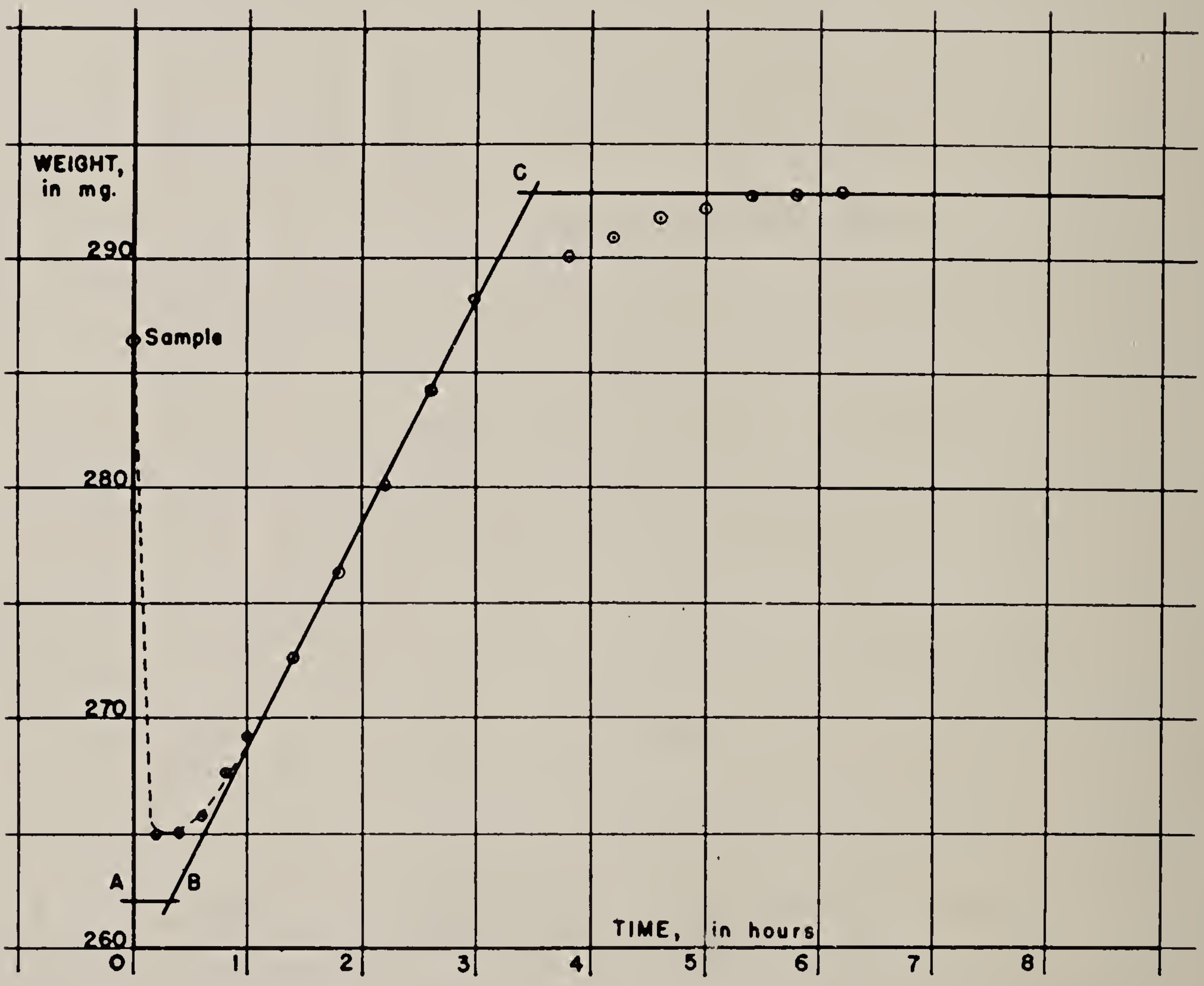


Fig. IV-1. Typical change in weight of linseed oil film on drying.

with drier. There is a rapid initial loss of weight due to evaporation of the volatile solvent introduced with the drier, followed by a steady gain as oxygen is absorbed. At the point *C* this straight line breaks as the film sets, polymerization having proceeded to gelation. The character of the compound determines whether there is a further slight gain or loss; linseed oil films usually lose, whereas materials which gel at lower levels of oxygen uptake continue to gain slowly. The point *C*, obtained as the intersection of two straight lines, is important since it corresponds closely with setting to touch; it was taken as the correct set-to-touch point in Scofield's report, as being more accurately determinable than by feeling with the finger at intervals.

For most natural oils there is an appreciable "induction" period after film-laying during which they show practically no change in weight. This is due to the presence in these oils of minute proportions of antioxidants whose activity must first be nullified; it is represented in the curve by the portion *A–B*. Scofield found that for the synthetic compounds the induction period, if any, was so short that it was lost in the evaporation of the volatile matter.

Tests to determine the influence of varying film thickness (Table IV-1) indicated that it is not very critical over a fairly wide range, from 1 to 1.5 mils or probably more. Five runs at very nearly the same thickness show the reproducibility of results. Agreement is not perfect; some uncontrolled variable must have been operating, probably temperature, which has a marked effect. The unavoidable variation of at least 1 degree in the temperature of the room could

TABLE IV-1
Influence of Film Thickness on Gain in Weight

Thickness (mils)	Time (hr.) Induction	Set	Gain	Gain in weight %	%/hr.
2.19*	0.4	3.3	2.9	9.8	3.4
1.40	0.2	3.9	3.7	13.6	3.7
1.32	0.3	3.5	3.2	11.8	3.7
1.07	0.7	4.4	3.7	12.6	3.4
1.06	0.3	3.7	3.4	14.6	4.3
1.04	0.5	4.1	3.6	15.2	4.2
1.04	0.5	3.9	3.4	12.3	3.6
1.04	0.2	4.1	3.9	15.0	3.8
0.44*	0.2	4.3	4.1	18.5	4.5
Mean	0.4	3.9	3.5	13.6	3.8

* Not included in the mean.

TABLE IV-2
Influence of Temperature on Gain in Weight

Temperature (° C.)	Time (hr.)			Gain in weight	
	Induction	Set	Gain	%	%/hr.
22.53	0.6	5.9	5.3	13.8	2.6
22.53	0.5	3.6	3.1	12.8	4.1
29.00	0.3	3.1	2.8	12.2	4.3

TABLE IV-3
Influence of Air Circulation on Gain in Weight

	Time (hr.)			Gain in weight	
Air	Induction	Set	Gain	%	%/hr.
Normal	0.4	3.9	3.5	13.6	3.8
None	0.1	4.5	4.4	15.2	3.5

TABLE IV-4
Influence of Time Elapsed after Addition of Drier on Gain in Weight

	Time (hr.)			Gain in weight	
	Induction	Set	Gain	%	%/hr.
New	1.7	5.2	3.5		
1 day	0.4	3.8	3.4	12.8	3.7
2 days	0.6	3.6	3.0	12.4	4.2
2 weeks	0.4	3.9	3.5	13.6	3.8

TABLE IV-5
Influence of Light on Gain in Weight

	Time (hr.)			Gain in weight	
	Induction	Set	Gain	%	%/hr
15 foot-candles	0.4	3.9	3.5	13.6	3.8
150 foot-candles	0.3	3.7	3.4	12.9	4.0

account for this. The total gain in weight was not reproducible; it depended on rate of gain and time.

The influence of temperature is shown in Table IV-2, bearing out the general rule for chemical reactions that the rate doubles for a rise of 8° to 10° C. Decreasing air circulation (Table IV-3) by stopping the turntable and fan slows the rate of polymerization, so that duration of gain and total gain increase.

Table IV-4 shows how time elapsed after adding drier, before laying film, affects the oxidation. For the greatest efficiency of catalytic action, 24 hours appears necessary and probably sufficient, but 48 hours gives a margin of safety; this longer period was observed in the rest of Scofield's work.

A light intensity of 150 foot-candles, obtained by placing a fluorescent fixture immediately above the table, did not significantly hasten the reaction (Table IV-5). Darkness is generally agreed to delay it, but this question was unimportant in this investigation and was not further studied.

Pure Compounds

Oleic esters and alkyds did not gain during a reasonable period; rather, they lost at a rate of about 0.2% per hour. Ultimately this trend reversed. All behaved quite similarly and none except the short-oil PE alkyd, Compound 23, dried in the ordinary sense. No. 23 dried by solvent evaporation to a hard film, in the same manner as a nitrocellulose lacquer.

Esters Other Than Eleostearic

All the esters of linoleic and linolenic acids, and the varnish linseed oil, followed a uniform pattern, first losing weight with evaporation of solvent, then gaining steadily until the film set, finally losing very slightly. In Scofield's work, done before the hypodermic syringe was brought into use for drier addition, the accuracy of that addition to the small samples was not precise, so he determined the nonvolatile weight of the film by extrapolating to zero time; it averaged about 92% of the sample taken but varied slightly. He could not detect any significant induction period even in the case of the linseed oil; a very short one, obscured by loss of solvent, could not be entirely ruled out. Smoothed curves for these materials are shown in

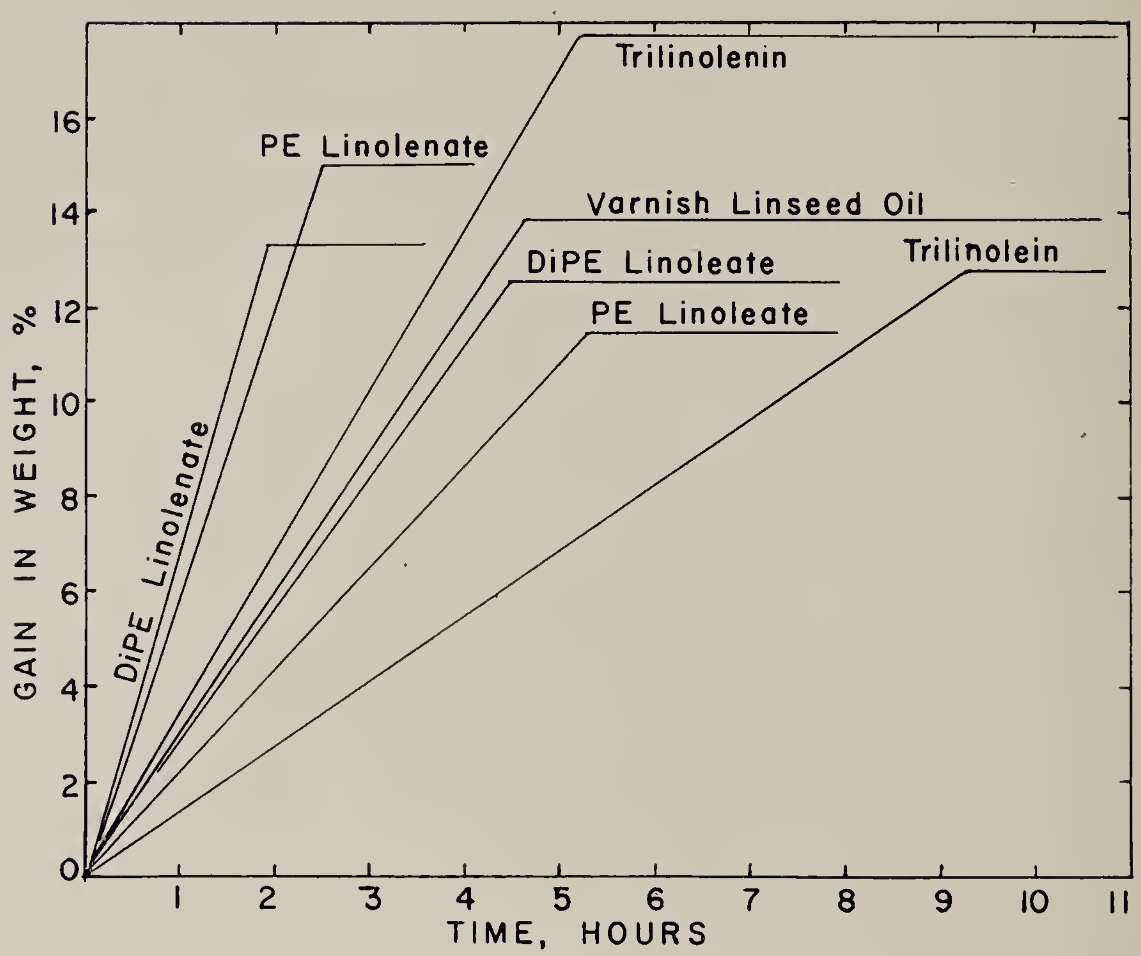


Fig. IV-2. Gain in weight of ester films based on weight of nonvolatile.

TABLE IV-6
Gain in Weight of Federation Vehicles

	Time to set (hrs.)	Gain in weight	
		%	%/hr.
Trilinolein	9.2	12.7	1.3
Trilinolenin	5.2	17.8	3.4
PE linoleate	5.2	11.3	2.2
PE linolenate	2.5	14.9	6.0
DiPE linoleate	4.4	12.8	2.9
DiPE linolenate	1.9	13.3	6.9
LO linoleic glycerol alkyd	2.2		2.4
LO linolenic glycerol alkyd	1.0		4.3
LO eleostearic glycerol alkyd	1.9		?
SO linoleic glycerol alkyd	3.5		1.0
SO linolenic glycerol alkyd	1.4		1.5
LO linoleic PE alkyd	2.7		1.9
LO linolenic PE alkyd	1.5		4.5
Varnish linseed oil	4.7	13.7	2.9

Fig. IV-2 and the setting time, gain in weight, and rate of gain are shown in Table IV-6. They are all in the expected order.

Eleostearic Esters

Within 15 minutes after application, these esters formed a wrinkled top skin which slowed up evaporation of solvent and absorption of oxygen. Gelation occurred before all possible oxygen was taken up, so that the films continued to gain after setting. The extrapolation method for determining solids weight at zero time could not be used, so nonvolatile content can only be estimated. Data for three runs of each sample and for two of dehydrated castor oil (for comparison) are plotted in Fig. IV-3, on the basis of weight of sample.

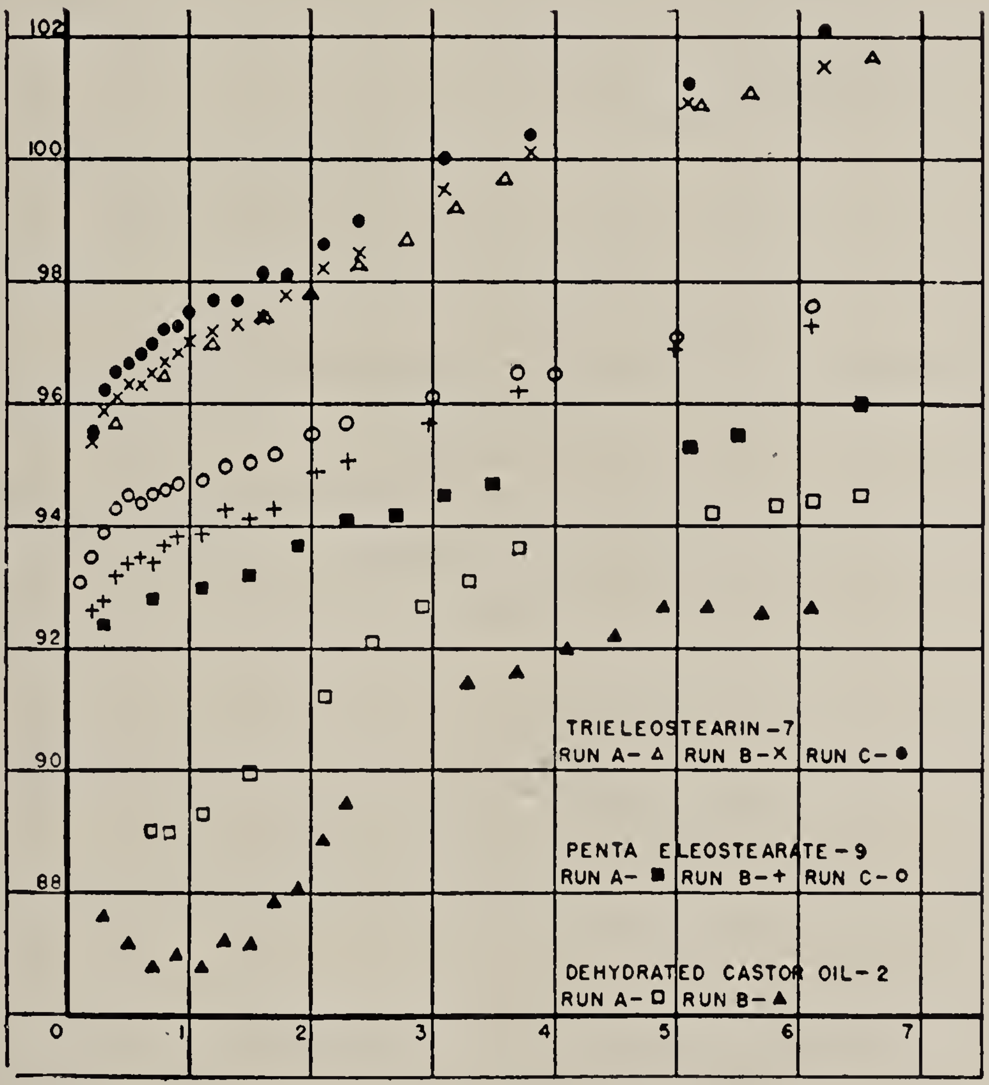


Fig. IV-3. Gain in weight of eleostearic ester and dehydrated castor oil films, based on weight of sample taken.

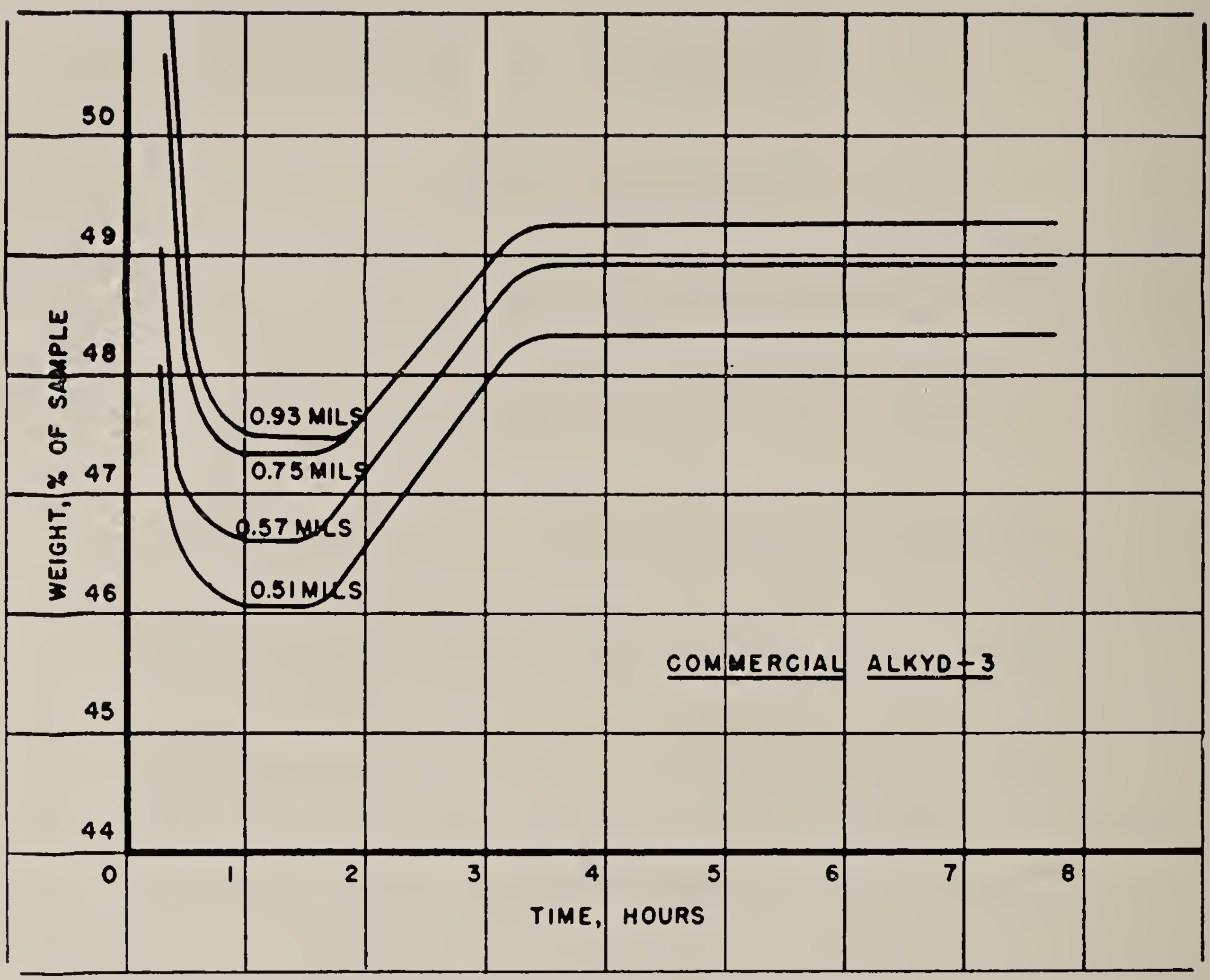


Fig. IV-4. Gain in weight of commercial alkyd films of different film thicknesses, based on weight of sample.

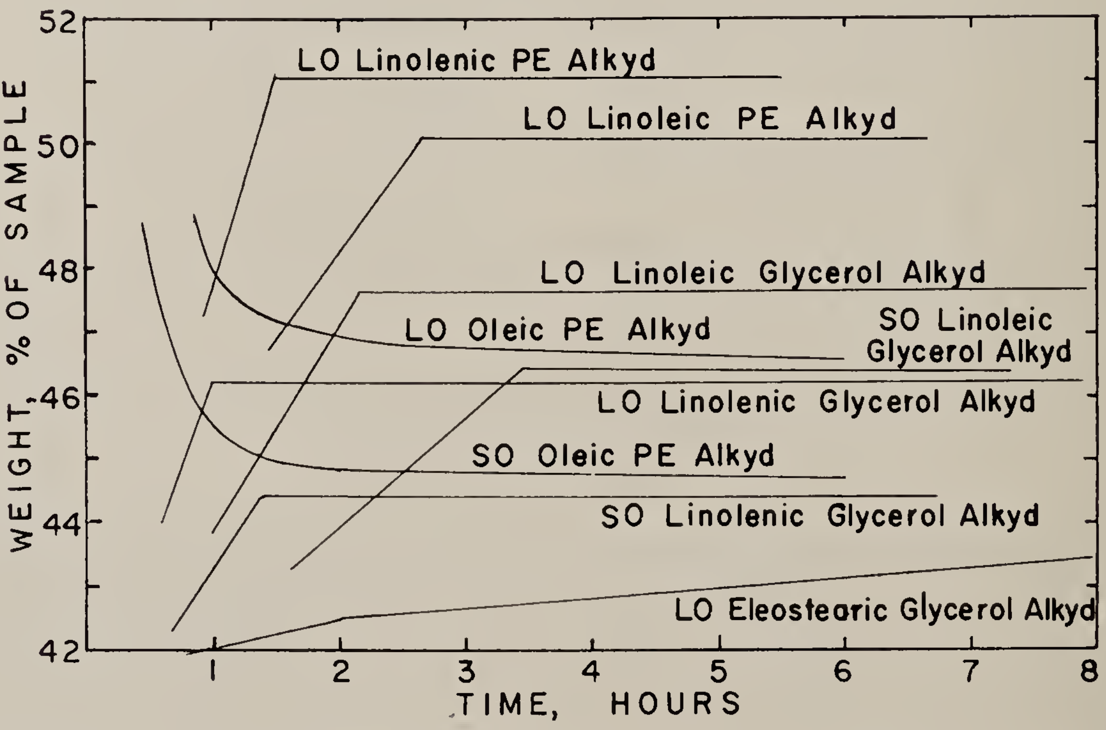


Fig. IV-5. Gain in weight of alkyd films, based on weight of sample.

Alkyds of Drying Acids

Here also, doubt as to the precise value of nonvolatile content and as to the existence of an induction period obscures the starting weight of solids; in some, evaporation of solvent clouds the whole setting period. To try to ascertain the influence of film thickness the commercial alkyd, Compound 3, was run at several thicknesses; results, based on original sample weight, are plotted in Fig. IV-4, where definite evidence of an induction period and a set-to-touch point appears. Film thickness affected the rate of solvent evaporation but no other properties examined in these tests. Thickness values given are approximate ones for the nonvolatile content. Figure IV-5 presents curves for the other alkyds, and Table IV-6 tabulates the data.

Gain in Weight, Project 1—Louisville Series

Duplication of some of the work on gain in weight at the two locations aids in judging the significance and reproducibility of the measurements. However, the emphasis differed, so that to a considerable degree the results of the two studies complement each other. Scofield added drier to all samples; he paid most attention to the early stages of the drying cycle (especially up to and immediately beyond the set-to-touch stage) and the factors that influence gain in weight.

In Williams' work the gain in weight was determined on films both with and without drier, and in the case of films with drier, both with and without an aging period after addition of drier to the compounds. Weights were taken at short intervals during the first hour, hourly for the rest of the first day, and at increasingly longer intervals for 90 days. Films with and without drier were also baked at 250° F. and weighed at intervals for 2 days. The specific gravity of films was measured after drying for 1 week, 1 month, and 3 months. Williams regarded the maximum percentage gain in weight, the time taken to reach this gain, and the set-to-touch time (determined by finger touch) as most significant, and he reported these for the air-dried films. The baked films lost weight continuously, and the loss after 50 hours was reported.

Experimental

The sample of compound was poured from the containing vial into a 25-ml. Florence flask, reduced to 50% nonvolatile by adding mineral spirits or other specified solvent, and stirred with the needle of a hypodermic syringe. For the tests with drier, 0.1 ml. of drier was added per gram of solids. Part of this sample was aged under vacuum for 24 to 48 hours before being used for air-drying tests; the rest of it, unaged, was used for the baking and some air-drying tests.

The glass photographic plates on which the films were to be laid were prepared by scraping off the emulsion after softening in hot water, washing alternately with aqueous detergent and acetone, immersing 24 hours in a nitric-sulfuric acid mixture, rinsing, brushing thoroughly with aqueous detergent, and drying. Immediately before use, they were wiped with cotton saturated with acetone and again wiped with a dry cloth.

For an area of 54 square centimeters it was calculated that a volume of oil of 0.38 ml. would provide a film of 1.25 mils thickness. This volume was deposited on the plate by means of a syringe graduated to 0.01 ml., and the oil was brushed out evenly over the area with an artist's brush previously saturated with the sample. If crawling occurred, the film was smoothed by continued brushing or by spreading with a finger tip.

The air-drying experiments were planned to be run in three sets, usually with four plates in each: (*1*) without drier, (*2*) with drier, not aged, (*3*) with drier, aged. It was intended to observe the normal 48-hour aging period for set (*3*), but there were some departures from this condition. This set was omitted entirely in the cases of trilinolein, trieleostearin, PE oleate, diPE linoleate, and diPE linolenate; also in the cases of all the alkyds, after it was found that the LO linoleic glycerol alkyd started to gel after about 30 hours. For PE linoleate, the aging period was 45 hours; for PE eleostearate, which was found to have gelled 48 hours after drier addition, the period was cut to 20 hours. Standard temperature and humidity were maintained, as well as the standard illumination of 25 foot-candles from fluorescent lights. A turntable (2 r.p.m.) and fan arrangement similar to that of Scofield was used. The plates were weighed on an analytical balance at intervals of 5, 10, 15, 20, 30, 45, and 60 minutes, at hourly intervals for the rest of th day, and at the end of 1, 2, 3, 7, 10, 21, 30, 45, 60, and 90 days.

Baking experiments were in two sets, with two or three plates for each: (*1*) without drier, (*2*) with drier, unaged. For compounds 5 and 7 to 14, inclusive, the panels were baked at 250° F. in a Sargent electric drying oven, from which they had to be removed, then cooled, weighed, and replaced—a technique that proved unsatisfactory because of variable weight changes during the cooling and reheating periods. The rest of the plates were baked in a forced-convection electric oven with a balance arranged so that they could be weighed without being removed. Weights were determined at the same intervals as for the air-dried films up to the end of the second day.

For specific gravity measurements, portions of films of about 10 to 20 mg. were scraped from the plates and immersed in a 2% water solution of Tergitol in a specific gravity bottle. Without this wetting agent, it was almost impossible to remove air bubbles. Three or four determinations were made each time, and the average of these was reported. The density of the Tergitol solution was practically the same as that of water.

In plotting on semilogarithmic paper the data from the air-drying tests, it was observed that there was an initial loss due to solvent evaporation, and that before a gain in weight set in, the film weight remained nearly constant at the minimum for a short period. It was assumed that up to this point the solvent vapor blanketing the film prevented access of oxygen to it so that no absorption of oxygen had occurred. This assumption is not entirely justified but experience indicated that it leads to no great errors. On this assumption, all the data were converted to a basis of 100 mg. of nonvolatile compound calculated from the weight at the minimum point on the curve; or in other words, to percentages of that minimum weight. The points plotted on the graphs are average values from three or four plates; individual values which vary significantly from the average are indicated by a vertical line.

Gain in weight from the minimum values continued until a maximum was reached; the trend then reversed, and the films were still losing weight after three months.

In the baking tests, the films seldom showed any gain. Almost all lost weight rapidly at first with release of solvent, but after 5 to 10 minutes the rate slowed markedly. At the end of the first hour the loss became much more gradual as the tack-free stage was reached. The slight losing trend persisted for 50 or 100 hours. It was assumed that practically all solvent was driven off in the first 5-minute interval, and that no other reactions involving weight change occurred in that period; therefore all data were converted to a basis of 100 units of oil calculated from the weight of film at the end of the period (or to percentages of that weight). Averages from two or three runs are plotted in the graphs, vertical lines indicating individual variations from the average.

A number of the pure esters, and even the varnish linseed and dehydrated castor oils, gave trouble by crawling when applied without drier. Especially was this true with trilinolein (which would not stay in place until after 20 hours), PE oleate and linoleate, and diPE oleate and linoleate. The simple oleic esters crawled to some extent even with drier added; they failed to dry and gained no appreciable weight; however, the oleic alkyds dried and also gained weight. The eleostearic compounds tended to skin over quickly or to gel soon after the ampules were opened; the short-oil eleostearic glycerol alkyd, Compound 19, had gelled before it was received, and could not be used. The simple eleostearic esters, especially when laid without drier, quickly formed the frosted, finely wrinkled skin characteristic of raw tung oil. This skin retarded oxygen absorption, and the gain in weight was correspondingly slight for these vehicles. The results from both the oleic and the eleostearic series of compounds should therefore not have too much significance attached to them.

The data appear in Tables IV-7 to IV-29, and those for a few selected compounds are shown graphically in Figs. IV-6 to IV-19. These data are average values of three or four individual tests calculated in percentages. The maximum percentage weight gain, the time taken to reach it, and the set-to-touch time for all the air-drying tests are shown in Tables IV-30 to IV-32. Table IV-33 presents losses for baked films at 50 hours. There is also a table (IV-34) of specific gravities of films at three ages. The samples used were too small for high accuracy, but the results indicate generally that there is an increase with time; no valid conclusions can be drawn.

Figure IV-20 shows a comparison between data obtained by Scofield on trilinolein and those reported by Williams for the same compound when recalculated to the same base. Agreement is, in general, very satisfactory. Table IV-35 presents a comparison between the per cent gain in weight and the set-to-touch time for those compounds for which the results from the two laboratories are comparable. The major part of the observed discrepancies arises from a gain in weight of alkyds after they set to touch, found by Williams but not by Scofield. The method of determining the base nonvolatile content probably erred for these materials which set so quickly; the figures therefore have questionable absolute value and should be used only on a comparative basis. In view of the highly empirical nature of the observations and the close control of the variables necessary, the agreement of many of the results is surprisingly good.

General Trend of the Results

As expected, the linolenic esters set to touch faster than the linoleic; they show a somewhat faster and larger gain. The greater number of points at which oxygen can react accounts for this. In a comparison of the alcohols, glycerol esters take the longest time to dry and attain the highest maximum weight. PE esters have a higher rate and diPE are fastest, more rapid gelation going hand in hand with higher functionality. Differences in weight gain are slight; earlier gelation offsets the faster rate. In general the alkyds, partially polymerized before starting and with slightly higher functionality, need little weight gain to bring about fast gelation.

Scofield's results on rate of gain (Table IV-6) demonstrate both the increase corresponding with the higher functionality of alcohol and the relation that, in passing from linoleic to linolenic esters, the rate more than doubles for an increase of 100% in the number of methylene groups that are highly activated by having two double bonds adjacent to them. In considering the alkyds it must be remembered that because of the phthalic content these compounds contain less of the various acids than do the simple esters; the rate of oxidation and the total gain are correspondingly lower.

Williams' comparisons between oils with and without drier show that whereas the latter took longer to set and in general gained more, the shapes of the curves are very similar; drier speeds the reaction but does not change the mechanism. The slow but steady loss with age after passing the maximum weight indicates a loss of scission

Tables IV-7 to IV-35 and Figs. IV-6 to IV-20 follow.
Text continues on page 76.

TABLE IV-7

Trilinolein Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	15	103.5	0	15	107.2	0	5	100.0	0	5	100.0
0	30	100.4	0	30	102.5	0	10	94.4	0	10	98.8
0	45	100.0	0	45	101.6	0	15	92.7	0	15	98.9
1	00	100.1	1	00	101.4	0	20	90.9	0	20	98.0
1	15	100.3	1	30	100.8	0	30	90.3	0	30	95.3
1	45	100.9	2		100.6	0	45	89.1	0	45	93.3
2	15	101.5	2	30	100.6	1	13	86.2	1	00	89.8
3	15	102.8	3	30	100.5	3		85.7	1	30	86.1
4	15	104.1	4	30	100.0	4	30	84.2	3	30	82.6
5	15	105.6	20		100.6	5		84.3	4		82.9
6	15	106.9	23	30	101.1	6		84.0	5		81.8
23		110.9	28		102.1	7		83.5	6		81.4
28		109.2	44		103.8	23		81.0	22		77.2
49		107.5	52		105.4	47		78.5	47		77.2
95		104.9	69		108.4				71		76.8
103		104.7	80		109.5						
119		104.1	95		113.7						
143		103.8	140		113.1						
168		103.3	149		112.5						
190		102.9	189		111.1						
263		101.8	211		109.5						
389		101.0	236		108.5						
462		100.0	308		106.6						
695		98.9	432		104.9						
1111		98.1	500		103.5						
1494		97.8	740		101.3						
2185		97.5	1153		100.0						
5472		95.9	1538		98.8						
			2204		98.9						

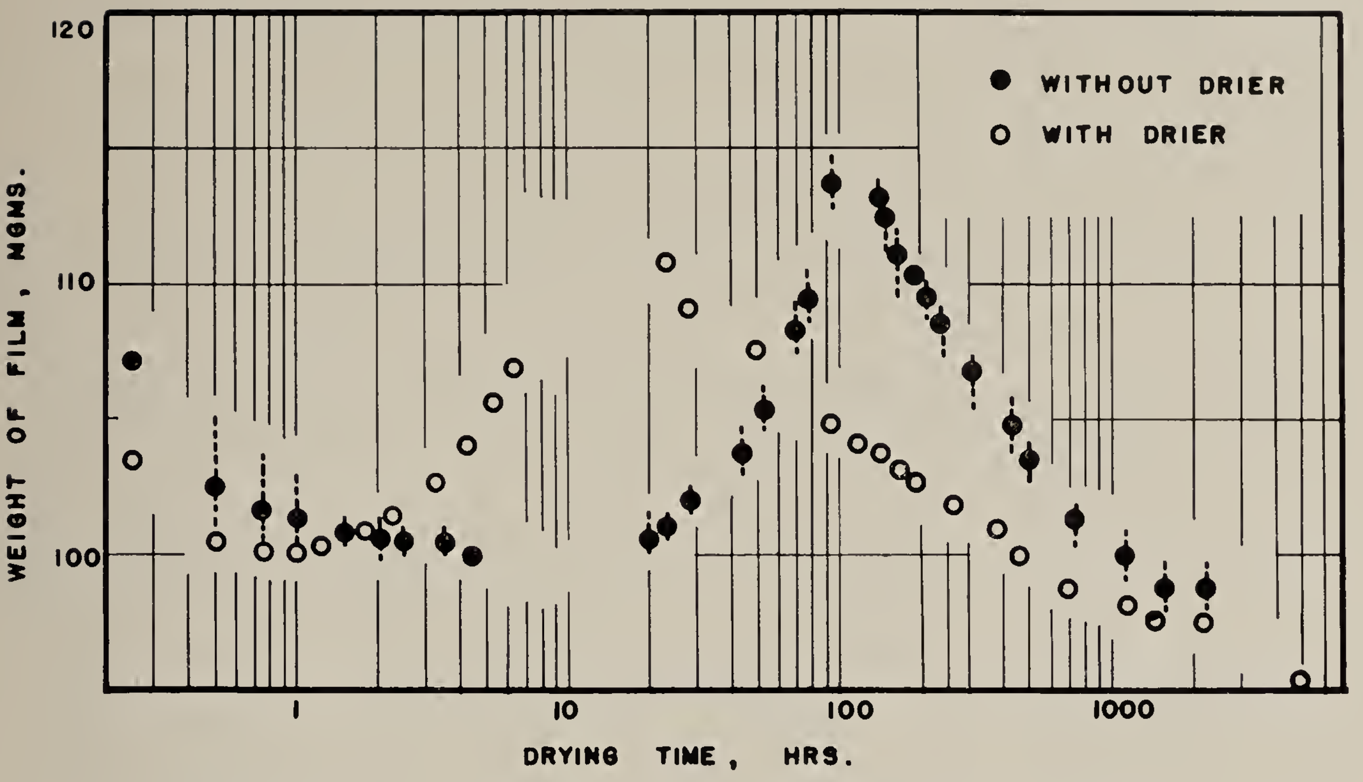


Fig. IV-6. Trilinolein films: weight changes on air drying.

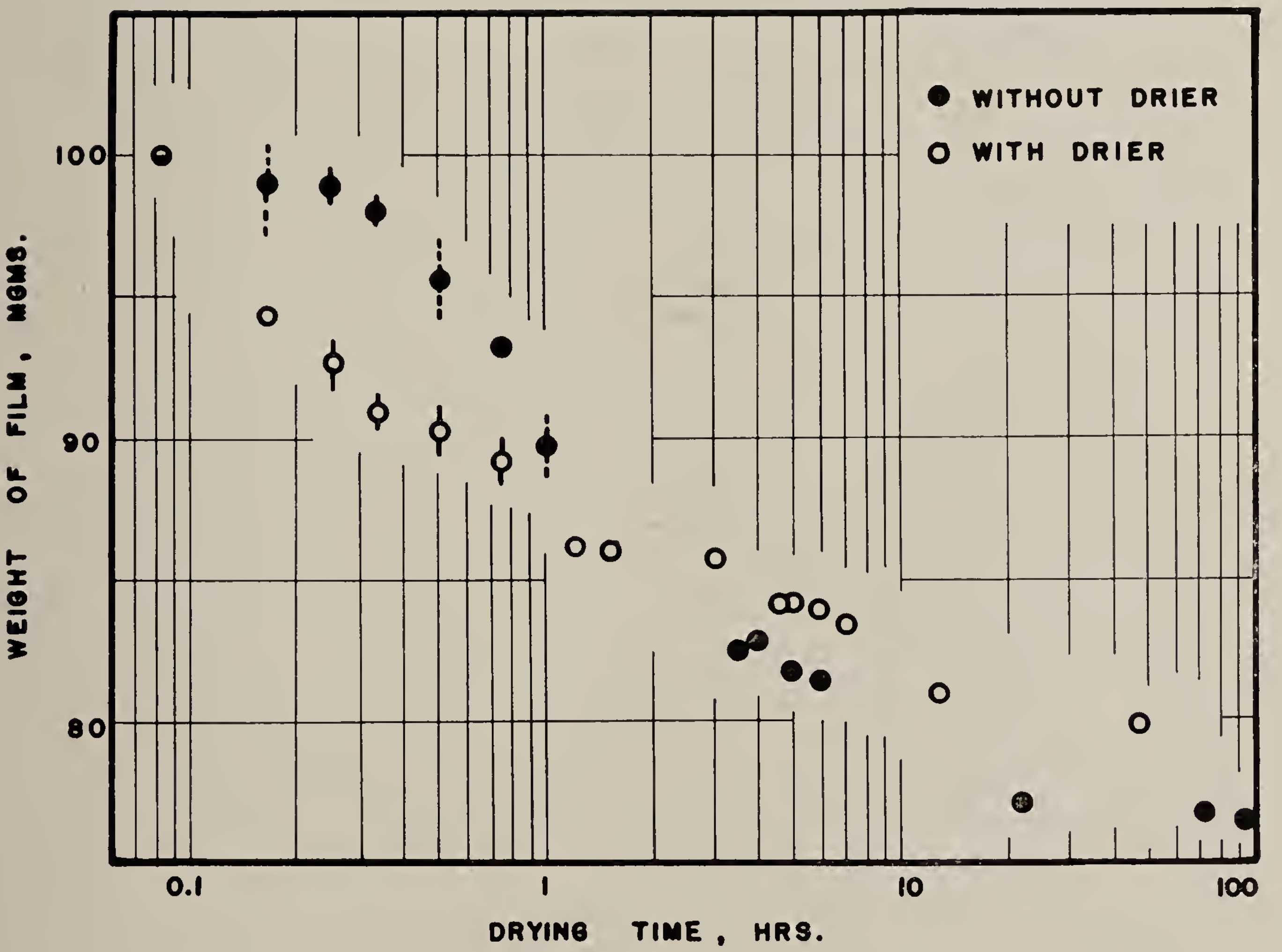


Fig. IV-7. Trilinolein films: weight changes on baking.

TABLE IV-8

Trilinolenin Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	10	113.0	0	15	108.7	0	5	100.0	0	5	100.0
0	20	101.5	0	30	101.8	0	10	96.2	0	10	101.9
0	30	100.0	0	45	100.5	0	15	95.2	0	15	101.2
0	40	100.3	1	00	100.0	0	20	95.5	0	20	100.6
0	50	101.1	2		100.0	0	30	94.2	0	30	98.1
1	00	102.4	3		100.2	0	45	92.6	0	45	95.6
1	15	105.1	4		100.3	1	25	91.9	1	00	94.9
1	30	105.6	16	30	103.4	3		91.2	2	30	93.7
2	8	109.0	18	30	104.4	4		91.1	4		92.3
2	15	109.2	22		106.1	5		90.1	6		91.1
2	30	110.0	25		107.9	6		90.2	23	30	85.5
2	45	110.6	28		110.1	23		87.2	69		83.7
3		110.6	41		119.0	48		86.5	92		83.0
3	15	110.9	43		119.1	73		85.3			
3	30	110.9	47		119.1	94		85.8			
4		110.7	49		119.1						
5		110.6	65		118.6						
6		110.3	116		118.0						
7		110.3	162		117.4						
23		110.0	212		116.9						
47	30	110.2	257		116.0						
121		110.3	504		114.2						
143	30	110.5	690		113.3						
168		109.9	1081		111.9						
193		110.3	1412		111.6						
238		109.8	2208		110.2						
485		108.9									
672		108.1									
1080		107.3									
1488		107.2									
2184		106.3									
5016		105.3									

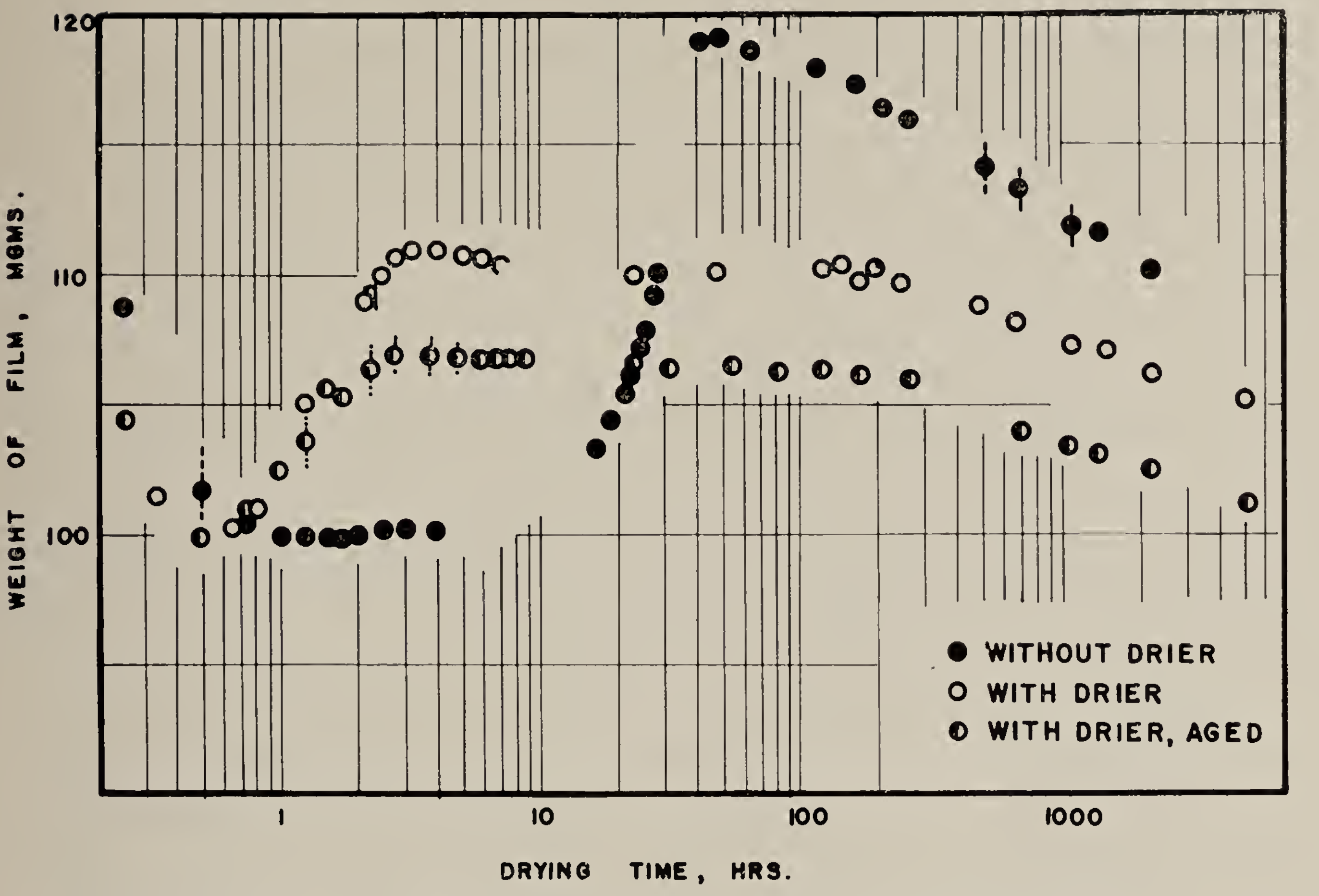


Fig. IV-8. Trilinolenin films: weight changes on air drying.

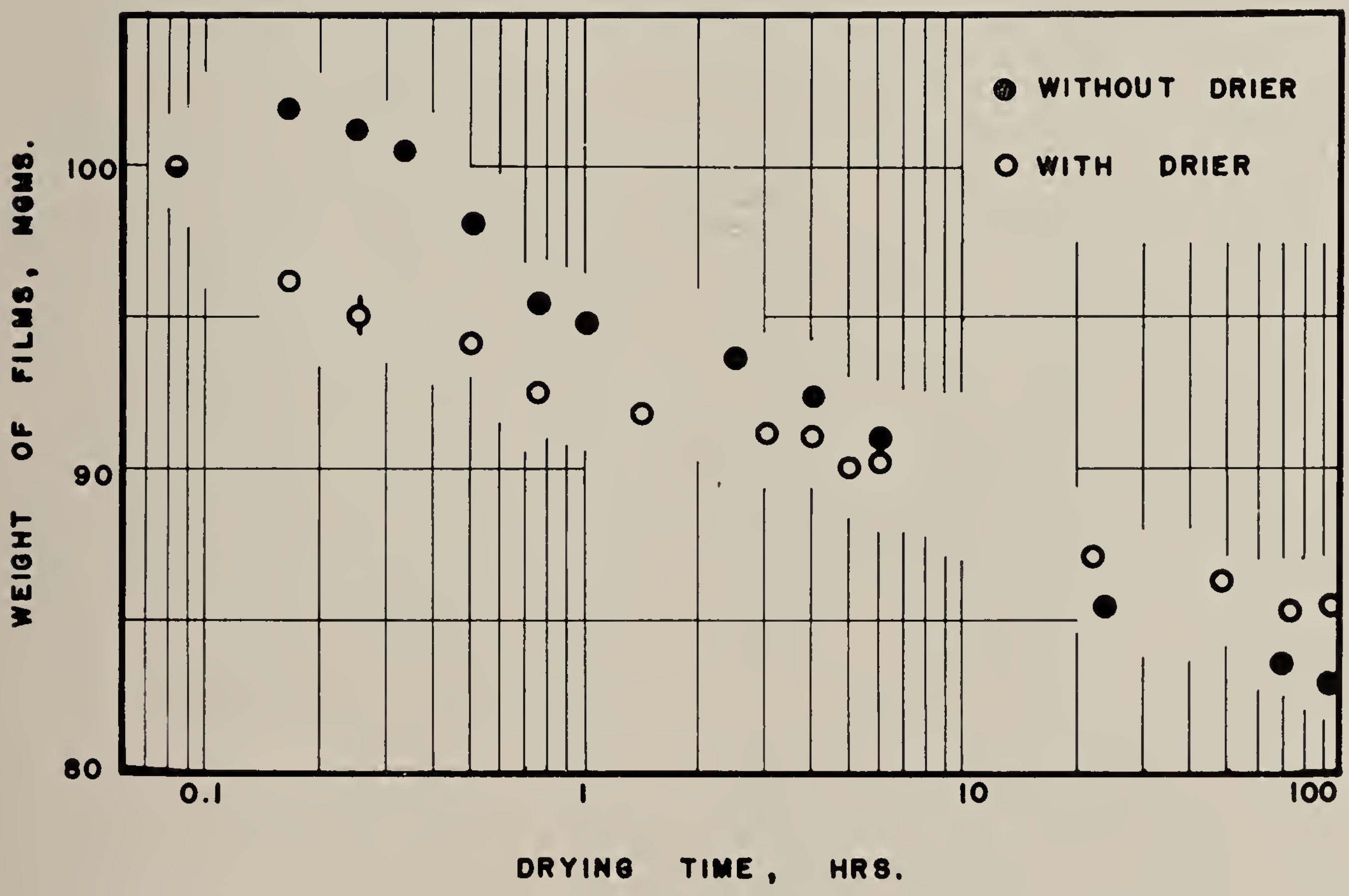


Fig. IV-9. Trilinolenin films: weight changes on baking.

TABLE IV-9
Trieleostearin Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	15	100.6	0	15	104.6	0	10	100.0	0	10	100.0
0	30	100.0	0	30	100.8	0	20	100.6	0	20	100.9
0	45	100.0	1		100.0	0	33	96.4	0	30	99.8
1		100.1	1	15	100.3	0	40	95.2	0	40	98.6
1	15	100.0	1	30	100.6	0	50	96.1	0	50	97.9
1	45	100.0	1	45	101.2	1		95.3	1		96.3
2	45	100.0	2		101.6	1	15	94.6	1	15	97.9
3	45	100.3	2	30	103.1	1	18	93.8	1	18	98.2
4	45	100.1	3	30	105.9	1	45	96.1	1	54	97.3
5	45	100.4	4	30	106.8	2	15	95.2	3	20	96.5
24		100.2	5	30	107.4	2	45	95.1	4		96.6
70		99.3	6	30	107.8	7	45	91.6	5		96.3
94		98.6	24	30	110.5	23	30	88.2	7		95.2
120		98.5	71		110.3	26	45	87.3	22		93.1
142		98.5	94	18	109.7	34		85.7	25		92.7
166		98.4	118	18	109.8	96		79.7	30	30	92.3
240		97.7	143		109.4	102		79.5	46		90.7
291		97.3	166		108.9	122		79.0	48	18	90.7
407		97.2	245		107.9	149		77.5	55		90.1
600		96.0	291		107.4	216		76.2	119		87.9
1080		95.1	411		106.8				125		87.5
1464		94.8	600		105.5				145		87.0
2160		94.3	1081		104.1				171		86.4
4944		93.5	1464		103.8				240		85.5

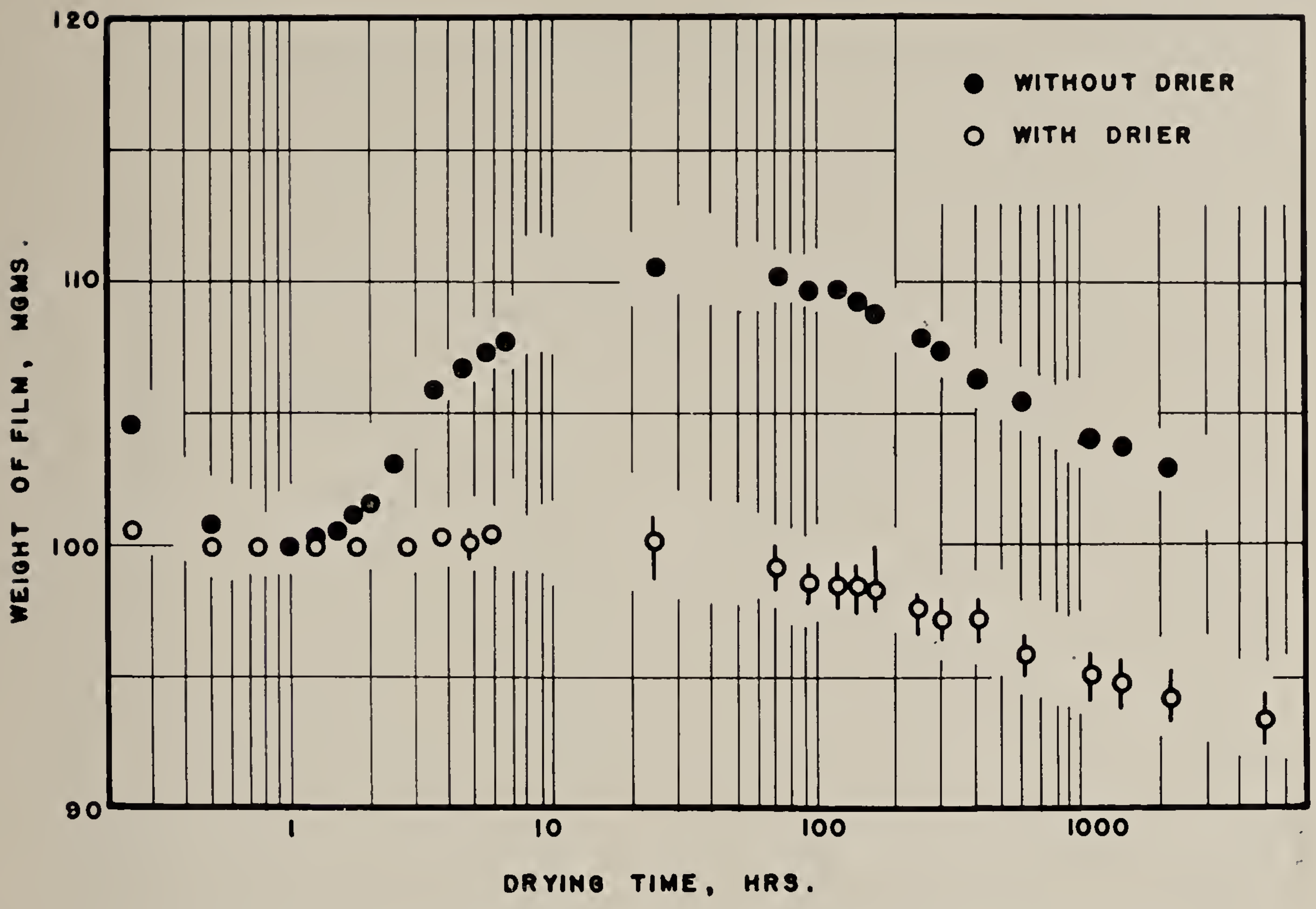


Fig. IV-10. Trieleostearin films: weight changes on air drying.

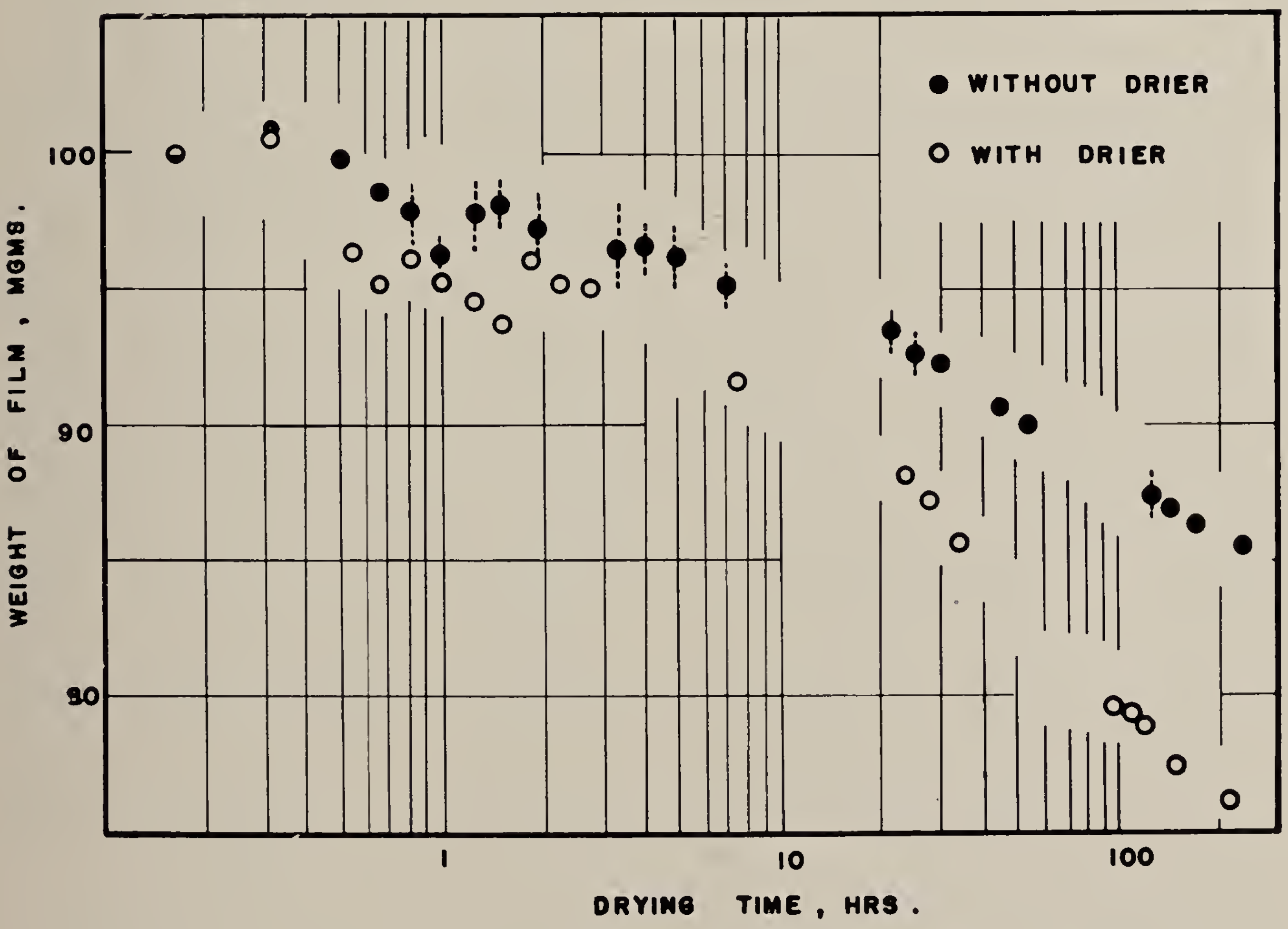


Fig. IV-11. Trieleostearin films: weight changes on baking.

TABLE IV-10

PE Oleate Films: Progressive Changes in Weight on Drying; Baked

With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	10	100.0	0	10	100.0
0	20	95.5	0	20	99.4
0	30	91.6	0	30	99.1
0	45	85.6	0	45	99.1
1		81.1	1		98.1
1	15	78.8	1	37	97.0
1	45	75.0	1	55	96.3
2	15	70.9	2	30	95.3
3	45	64.9	2	45	94.4
5	15	64.6	3		93.9
17	45	63.3	3	15	93.5
21		61.8	4	15	91.5
24	30	62.1	6		87.2
26		61.4	7	30	79.5
44		60.6	20		73.5
			23		73.1
			26	30	72.6
			28	30	72.3
			44	30	70.0

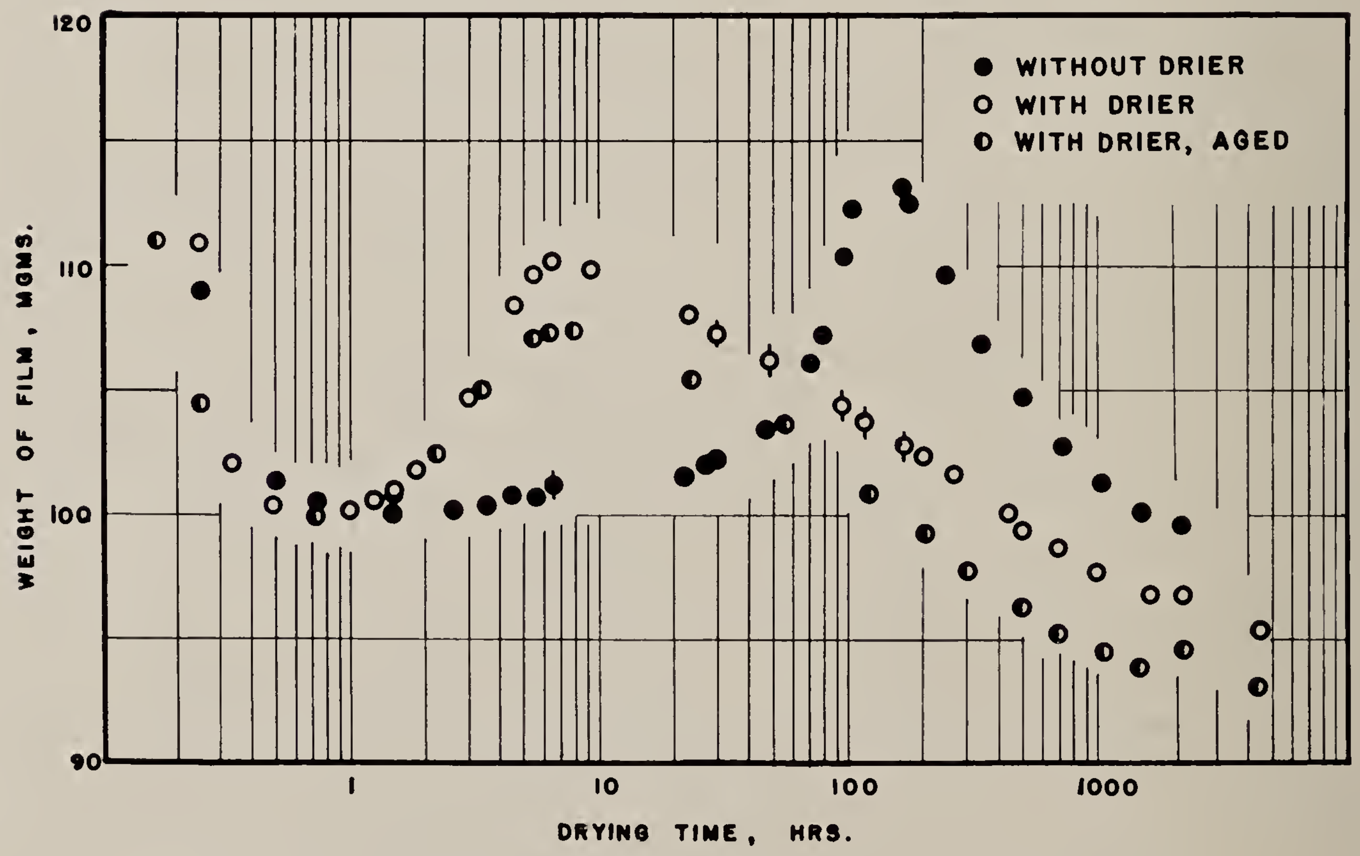


Fig. IV-12. PE linoleate films: weight changes on air drying.

TABLE IV-11

PE Linoleate Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	10	111.0	0	15	108.0	0	5	100.0	0	5	100.0
0	20	102.1	0	30	101.4	0	10	100.6	0	10	99.6
0	30	100.4	0	45	100.6	0	20	102.0	0	20	98.6
0	45	100.0	1		100.3	0	30	102.1	0	30	95.8
1		100.2	1	30	100.0	0	40	95.7	1	30	92.3
1	15	100.6	2	36	100.2	1		95.2	2	30	91.7
1	30	101.3	3	30	100.4	2		91.8	3	30	92.1
1	45	101.8	4	30	100.8	3		90.2	4	30	91.8
3		104.6	5	30	100.8	4		89.7	69		89.3
4	30	108.6	6	30	101.2	5		88.5			
5	30	109.6	22		101.6	69		82.7			
6	30	110.2	24		102.1						
9		109.8	26		102.1						
23		108.1	29		102.2						
29	30	107.4	47		103.5						
49		106.3	71		106.2						
96		104.5	79		107.3						
120		103.8	95		110.5						
166		102.8	103		112.4						
198		102.4	168		113.2						
264		101.7	174		112.5						
437		100.0	246		109.6						
505		99.4	341		106.8						
700		98.8	510		104.8						
1001		97.7	720		102.8						
1634		96.9	1084		101.4						
2182		96.9	1510		100.0						
4464		95.4	2184		99.6						

TABLE IV-12. PE Linolenate Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	15	107.5	0	15	114.5	0	5	100.0	0	5	100.0
0	30	100.4	0	30	102.8	0	10	100.6	0	10	100.9
0	45	100.0	0	50	100.6	0	15	100.1	0	15	102.5
1		101.2	1		100.6	0	20	99.5	0	20	104.5
1	15	102.5	1	30	100.1	0	30	99.2	0	25	106.4
1	30	104.0	2		100.0	0	40	99.2	0	30	107.4
2	50	108.2	3		100.1	0	50	98.6	0	40	107.7
3	50	108.3	5		100.4	1		98.5	0	50	106.7
6	30	108.0	6		100.7	1	30	97.9	2		102.8
23	30	108.1	7		100.6	2		97.3	3		101.2
100		108.2	8		100.9	19	30	94.0	4		100.8
169		108.5	11		102.0	27		93.7	5	30	100.1
265		108.6	23	30	112.0	45		93.2	20		98.0
336		108.7	25		114.0				28		97.6
504		108.3	26		115.0				48		96.1
767		107.7	27	30	116.2						
1294		106.9	29		116.9						
1464		106.5	30		118.0						
2184		106.6	32		118.4						
4200		105.6	47		119.0						
			55		119.1						
			150		117.9						
			240		116.9						
			336		116.3						
			505		115.3						
			746		114.5						
			1344		113.2						
			1492		112.4						
			2212		112.3						

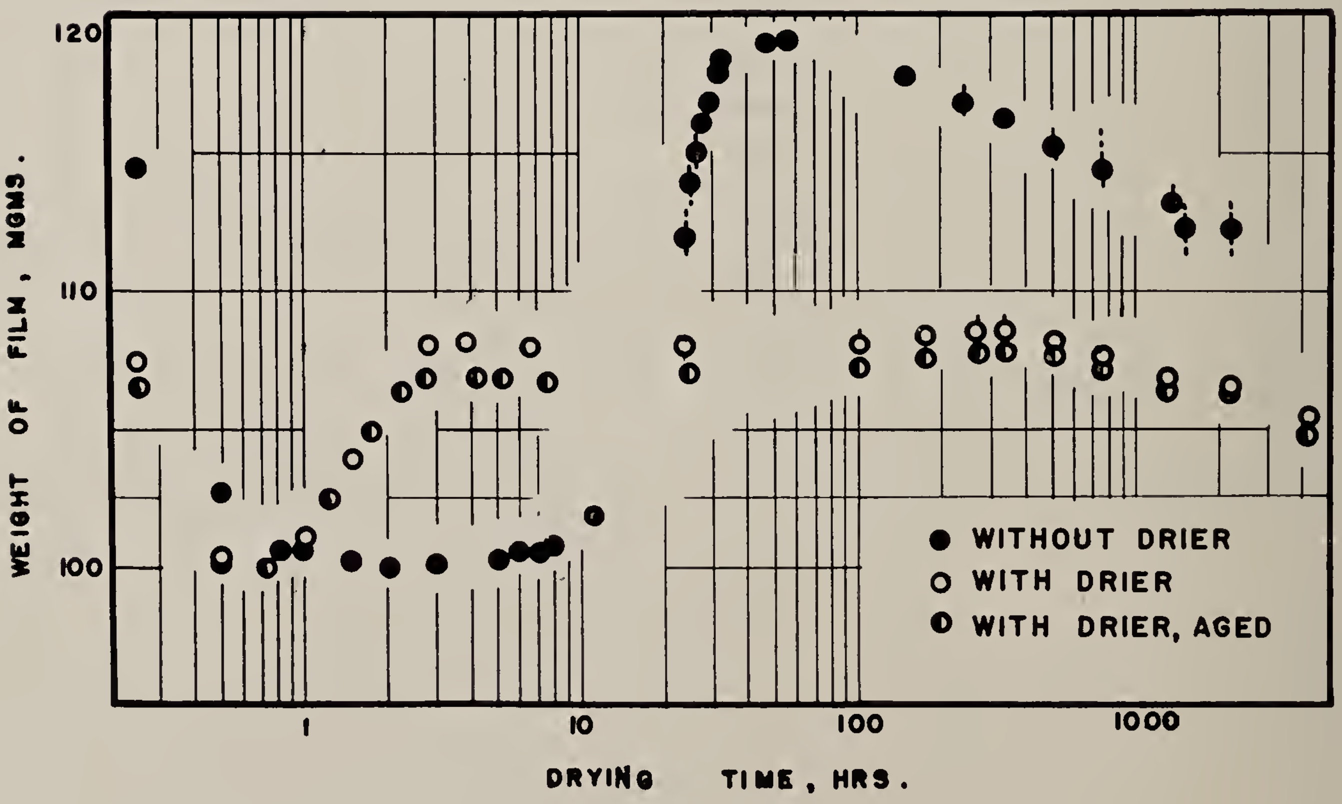


Fig. IV-13. PE linolenate films: weight changes on air drying.

TABLE IV-13

PE Eleostearate Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	10	110.6	0	15	110.9	0	5	100.0	0	5	100.0
0	20	100.4	0	30	101.3	0	10	100.0	0	10	101.0
0	30	100.3	0	45	100.4	0	15	99.7	0	15	101.4
0	45	100.0	1		100.0	0	25	99.5	0	20	101.6
1		100.3	1	15	100.0	0	36	99.1	0	25	101.6
2		100.1	1	30	100.2	1		97.6	0	30	101.8
4		100.0	2	40	101.3	2	30	96.7	0	45	101.0
5	30	99.7	3	38	103.7	3	45	95.4	1		100.1
24		97.6	4	30	105.3	5	45	95.0	2		98.5
72		95.9	5	30	106.5	23		92.7	3	30	97.5
97		95.4	6	30	107.1	29		91.6	4	45	97.0
170		94.8	22		110.6	94		89.7	26		95.2
240		93.7	25		111.2				47		94.3
308		93.3	30		111.4						
508		92.4	48		111.9						
684		92.2	73		112.0						
1104		91.1	170		110.9						
1464		90.7	220		110.1						
2280		90.2	337		108.9						
			528		108.5						
			721		107.7						
			1152		106.1						
			1468		105.9						
			2212		105.9						

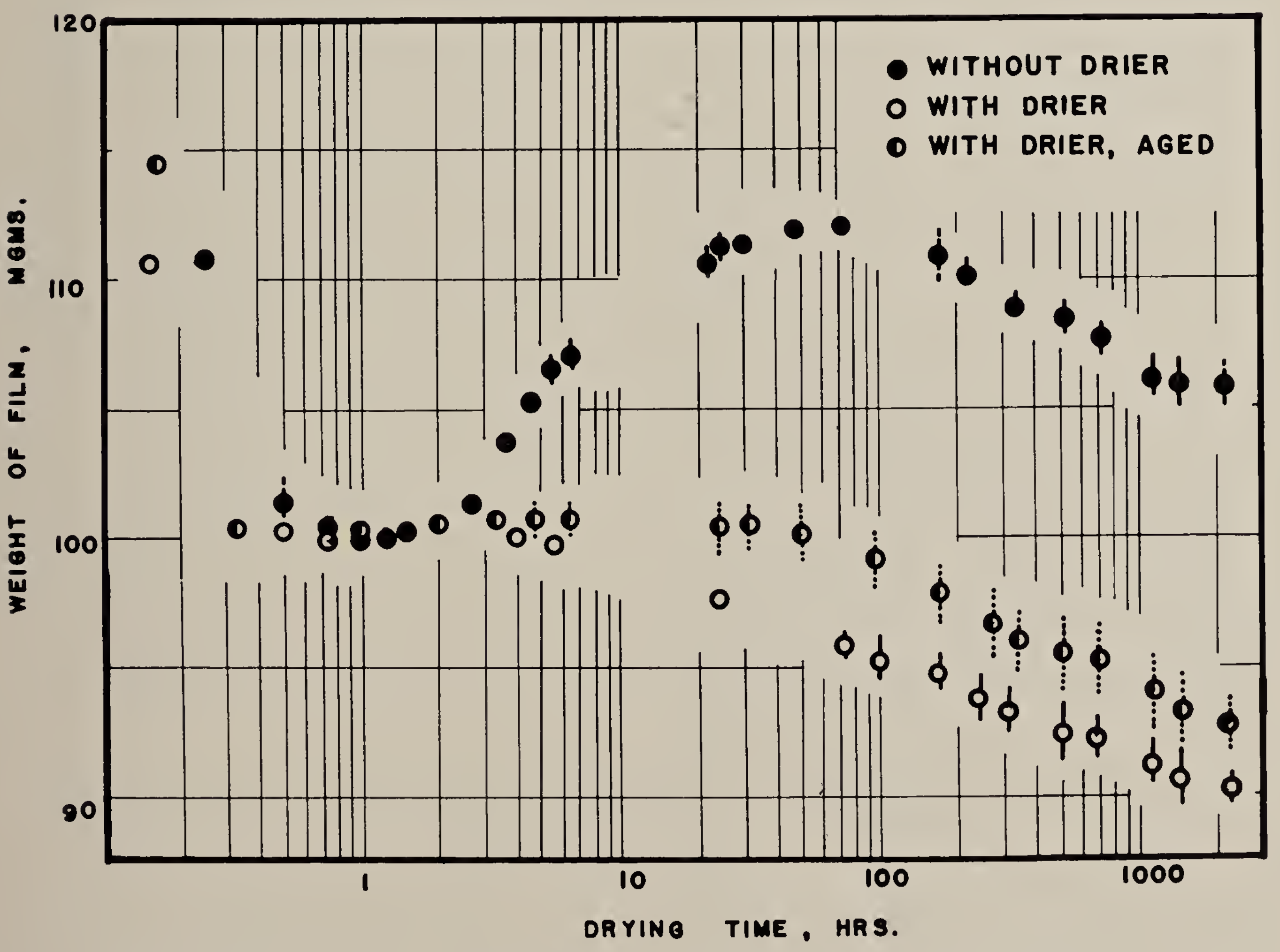


Fig. IV-14. PE eleostearate films: weight changes on air drying.

TABLE IV-14

DiPE Oleate Films: Progressive Changes in Weight on Drying; Baked

With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	5	100.0	0	5	100.0
0	10	99.5	0	10	99.3
0	20	98.8	0	15	99.0
0	30	97.8	0	25	100.0
0	45	96.6	0	40	99.6
1	30	91.2	1		98.6
3		82.2	1	30	97.8
5		76.9	2	30	96.1
22		61.1	3	30	94.9
46		55.3	4	30	92.4
			6		89.3
			22		79.6
			48		76.9

TABLE IV-15

DiPE Linoleate Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	10	121.9	0	15	123.8	0	5	100.0	0	5	100.0
0	20	106.8	0	30	114.0	0	10	100.2	0	10	98.1
0	30	101.4	0	45	109.2	0	15	99.6	0	15	97.9
0	45	100.0	1		105.1	0	20	98.6	0	20	98.0
1		100.1	1	9	104.0	0	30	97.6	0	30	99.4
1	15	100.1	1	18	103.3	0	45	96.1	0	40	100.1
1	30	100.4	2		101.1	1		95.3	1		98.7
2		101.0	3		100.2	2		92.4	2		92.0
2	45	101.8	4	30	100.0	3		91.6	4		88.2
5	45	106.8	6		100.0	4		90.3	5		87.6
7	45	108.9	7	15	100.4	5		89.7	24	30	84.4
24		107.7	23	30	100.9	21	30	86.2	72		82.0
98		103.2	25	30	101.3	46		84.6			
145		101.7	29	30	101.6						
264		99.7	49		102.1						
362		98.6	55		102.9						
480		97.6	71	18	104.0						
962		95.9	97	18	106.6						
1104		95.5	144		115.0						
1464		94.9	167		112.5						
2208		94.8	217		108.4						
			362		103.7						
			504		102.2						
			1055		98.8						
			1464		97.6						
			2209		96.8						

TABLE IV-16

DiPE Linolenate Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	15	113.3	0	15	109.0	0	5	100.0	0	5	100.0
0	30	100.0	0	30	101.6	0	10	99.6	0	10	101.0
0	45	100.0	0	45	101.5	0	20	99.1	0	15	102.9
1		101.3	1		100.4	0	30	98.7	0	20	104.5
1	15	103.3	1	30	100.3	0	45	97.7	0	25	105.3
1	30	104.5	2		100.0	1		97.1	0	30	105.7
2	30	107.3	2	30	100.1	1	30	96.7	0	40	105.3
3	30	107.3	3	30	100.1	2	30	96.6	0	50	105.2
4	30	107.3	19		104.2	4	30	95.8	1		104.5
5	30	107.2	24		107.5	6	30	95.6	2		101.3
23		107.3	45	30	117.7	47	30	93.3	3		100.1
48		107.4	68	30	117.7				5		98.6
78		109.0	117		117.8				21	30	96.5
241		109.4	165		117.6				45	30	94.8
335		109.8	331		117.1						
384		110.6	816		116.5						
408		110.5	1128		114.5						
844		110.4	1468		114.4						
1080		109.5	2208		113.7						
1488		109.5									
2232		109.2									

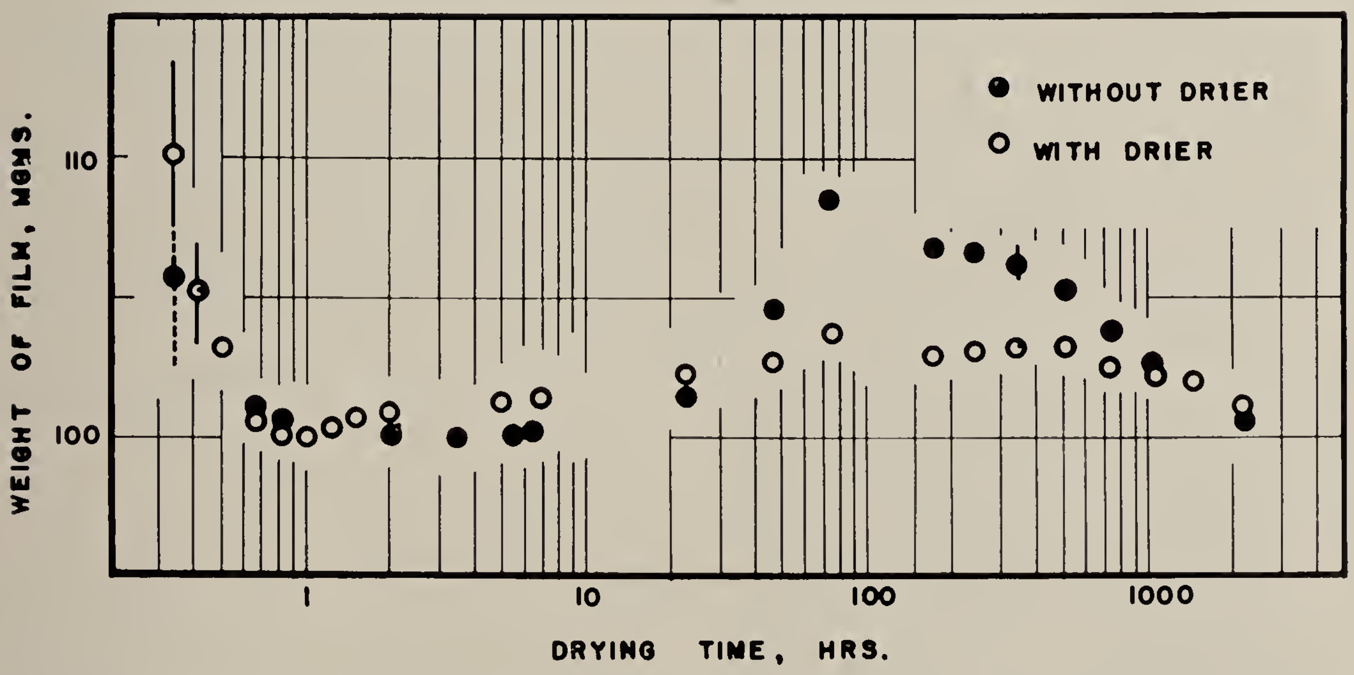


Fig. IV-15. LO linoleic glycerol alkyd films: weight changes on air drying.

TABLE IV-17
LO Linoleic Glycerol Alkyd Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	5	150.0	0	5	149.0	0	5	100.0	0	5	100.0
0	10	132.6	0	10	125.1	0	10	97.5	0	10	99.3
0	15	120.1	0	20	105.8	0	15	96.7	0	15	100.0
0	20	110.1	0	30	103.1	0	30	95.5	0	20	99.7
0	25	105.3	0	40	101.1	1		94.1	0	30	100.9
0	30	103.2	0	50	100.6	1	30	92.8	0	40	100.1
0	40	100.6	1		100.3	2	30	91.8	1	20	97.2
0	50	100.1	1	15	100.2	6	10	89.8	2	50	95.2
1		100.0	1	30	100.2	22		87.8	3		94.9
1	15	100.3	2		100.1	94		84.1	5		94.2
1	30	100.7	3	30	100.0				21		92.3
2		101.0	5	30	100.1				29	30	91.5
5		101.3	6	18	101.2				45		90.3
7		101.5	23		101.5						
23		102.3	48		104.6						
47		102.7	74		108.5						
74		103.7	172		106.7						
172		103.0	241		106.6						
241		103.1	340		106.3						
340		103.2	505		105.2						
504		103.2	745		103.8						
745		102.5	1081		102.6						
1080		102.3	1489		102.1						
1488		102.0	2207		100.6						
2208		101.2									

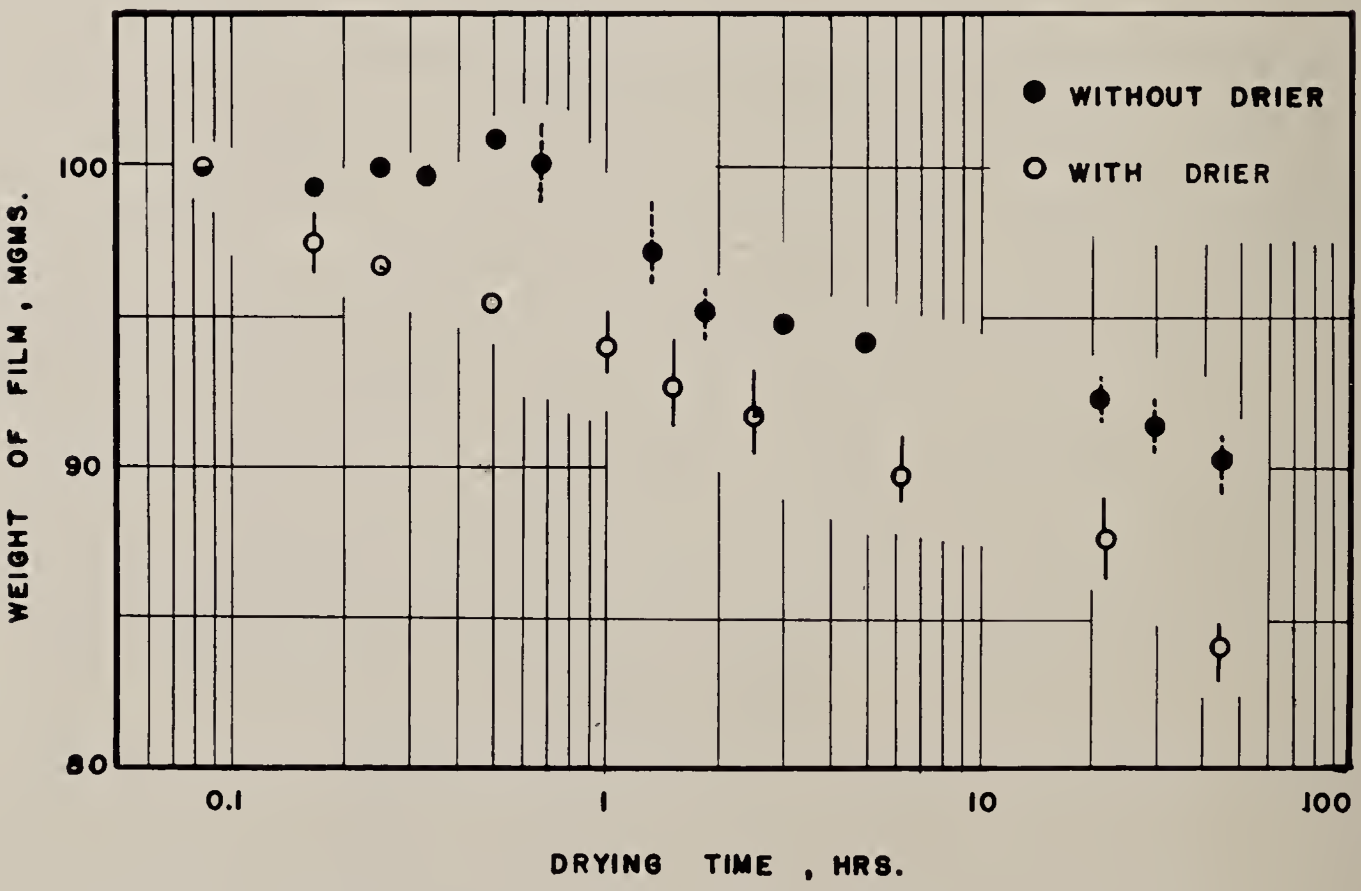


Fig. IV-16. LO linoleic glycerol alkyd films: weight changes on baking.

TABLE IV-18

LO Linolenic Glycerol Alkyd Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	5	147.2	0	5	139.5	0	5	100.0	0	5	100.0
0	10	129.6	0	10	124.6	0	7	95.9	0	7	94.1
0	15	114.2	0	15	119.6	0	10	92.7	0	10	93.8
0	20	106.1	0	20	108.0	0	15	87.8	0	15	94.2
0	25	102.3	0	25	104.7	0	20	85.5	0	20	94.4
0	30	101.0	0	30	102.7	0	30	84.0	0	25	93.8
0	40	100.4	0	45	100.6	0	45	80.7	0	30	93.7
0	50	100.0	1		100.3	1		79.0	0	45	91.7
1		100.2	1	30	100.1	2		77.2	1		90.9
1	30	100.3	2		100.0	3		73.6	3		90.6
2		100.3	3		100.1	4		69.7	19		85.9
3		100.4	22		105.7	6		68.4	42		82.6
5	30	100.8	44		106.3	21		63.4	92		78.2
24		101.0	68	30	106.7	46	30	60.0			
45	30	101.9	164	30	107.5						
70		101.8	261		107.7						
166		102.4	339		108.4						
266		103.2	500		108.6						
342		103.8	740		108.7						
502		104.3	1076		108.8						
746		104.9	1510		109.6						
1080		105.7	2227		109.6						
1508		106.1									
2230		106.5									

TABLE IV-19

LO Eleostearic Glycerol Alkyd Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	15	108.1	0	15	111.8	0	5	100.0	0	5	100.0
0	20	104.1	0	20	107.1	0	10	95.9	0	10	194.8
0	30	101.0	0	30	103.4	0	15	95.4	0	15	94.5
0	45	100.4	0	45	101.7	0	20	93.2	0	20	94.3
1		100.3	1		100.7	0	30	93.0	0	25	94.3
1	30	100.0	1	30	100.2	0	45	92.3	0	30	93.3
2		100.3	2		100.0	1		91.9	0	40	93.2
3		100.4	3		100.3	2		90.8	0	50	93.9
19		102.5	19		102.7	3		90.1	1		93.0
50		103.9	50		104.6	5		89.6	2		92.2
68	30	105.2	68		105.4	7		89.3	3		90.9
168		104.8	168		105.2	19	30	87.6	4		91.9
235		104.9	235		105.5	42	30	85.5	5		90.0
336		105.0	336		105.8				22		88.3
500		104.7	500		106.0				29		86.0
740		104.0	740		105.6				46		84.7
1076		103.2	1078		105.4				71		81.6
1488		103.2	1485		105.1						
2208		102.3	2203		104.8						

TABLE IV-20

SO Linoleic Glycerol Alkyd Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	15	110.8	0	15	110.6	0	5	100.0	0	5	100.0
0	20	105.2	0	20	108.1	0	10	93.8	0	10	100.0
0	30	101.9	0	30	103.3	0	15	91.5	0	15	98.8
0	45	100.5	0	45	101.3	0	20	90.0	0	30	97.6
1		100.0	1		101.0	0	30	88.1	0	45	96.6
2		100.5	1	30	100.5	0	45	87.6	1		95.0
3		101.0	2		100.2	1		87.0	2		94.9
4		101.8	3		100.0	1	30	84.7	3		93.9
5		102.1	4		100.3	2		86.3	4		93.0
28	30	102.5	5		100.1	3		84.3	5		93.6
46	30	103.9	6		100.3	69		75.6	6		92.7
165	30	103.5	29		101.7				7		92.7
292		103.5	71		105.2				72		86.4
363		103.9	166		105.4						
503		103.8	293		105.4						
792		103.5	363		105.6						
1128		102.7	503		105.1						
1488		102.6	792		104.7						
2208		102.3	1128		103.5						
			1486		103.1						
			1486		103.1						
			2206		102.7						

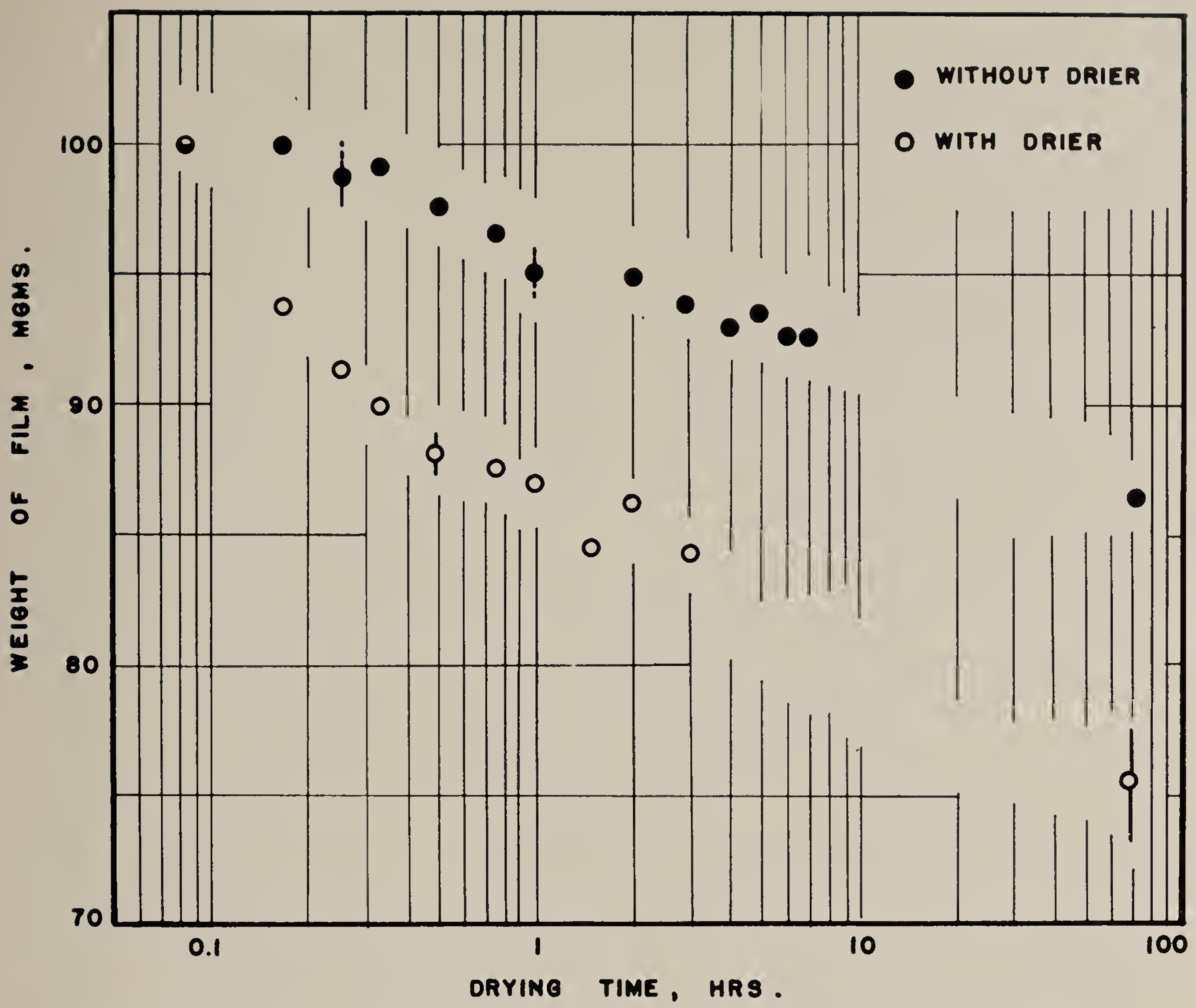


Fig. IV-17. SO linoleic glycerol alkyd films: weight changes on baking.

TABLE IV-21

SO Linolenic Glycerol Alkyd Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	15	112.5	0	15	109.8	0	5	100.0	0	5	100.0
0	20	106.2	0	20	105.8	0	10	95.5	0	10	98.4
0	25	103.4	0	25	103.7	0	15	94.7	0	15	98.5
0	30	101.8	0	30	102.4	0	20	94.4	0	20	98.8
0	45	100.3	0	45	101.1	0	30	93.8	0	30	98.3
1		100.0	1		100.6	0	45	93.7	0	45	98.3
1	30	101.0	1	30	100.2	1		93.4	1		95.7
2		101.1	2	30	100.0	2		92.4	2		96.3
3		101.3	25	30	100.7	3		91.5	19	30	93.3
4		101.3	115		104.3	4		91.9	44		92.2
23		102.4	163		104.6	6		91.4			
95		101.7	288		105.1	21	30	88.3			
171		102.0	360		105.5	24		88.0			
267		102.7	500		105.7	70		85.5			
363		102.9	787		106.1						
504		103.3	1123		106.6						
792		103.9	1483		106.8						
1176		104.6	2227		107.0						
1464		104.5									
2183		104.3									

TABLE IV-22

LO Oleic PE Alkyd Films: Progressive Changes in Weight on Drying

			Baked					
Air-dried, with drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	15	120.5	0	5	100.0	0	5	100.0
0	20	112.7	0	10	95.7	0	10	95.7
0	30	105.8	0	15	93.7	0	15	95.1
0	45	102.0	0	20	90.7	0	20	93.9
1		100.9	0	30	87.8	0	30	92.3
1	30	100.6	0	45	84.6	0	45	91.5
3		100.2	1		82.0	1		90.7
4		100.0	2		77.6	1	18	89.3
6		100.0	3	15	75.7	2		88.1
22	30	100.1	4		75.4	3		85.8
46	30	101.2	5		74.1	4		84.2
70	30	102.3	7		73.0	5		83.0
166	30	101.7	22		69.0	6		81.9
243		99.5	46	30	68.8	20		79.2
335		98.6				44		75.3
502		97.4						
744		96.8						
1176		96.3						
1488		95.4						
2207		94.9						

TABLE IV-23

LO Linoleic PE Alkyd Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	15	119.3	0	15	119.2	0	5	100.0	0	5	100.0
0	20	110.3	0	20	111.6	0	10	95.7	0	10	98.6
0	30	103.0	0	30	103.9	0	15	93.9	0	15	97.9
0	45	100.2	0	45	101.3	0	20	93.1	0	20	96.8
1		100.0	1		100.6	0	30	92.1	0	30	93.7
1	30	100.6	1	30	100.2	0	45	91.2	0	45	90.9
2		101.4	2	30	100.0	1		90.8	1		90.3
3		103.5	3		100.4	1	30	89.3	1	30	90.3
4		105.7	4		100.1	2		88.9	2		90.3
5		106.9	5		100.2	3		87.8	3		88.3
6		107.2	22		100.5	4		87.8	4		89.0
22	30	106.7	46		103.3	5		87.9	5		88.4
100		104.9	124		108.3	7		88.2	6		87.3
168		104.0	166		106.7	22		84.7	19		86.7
262	30	102.8	286		104.5	49		82.2	22		86.4
334		102.5	358		103.7				44	30	85.2
502		101.9	502		103.0						
768		101.4	742		101.5						
1104		100.3	1128		100.1						
1464		100.1	1464		99.6						
2206		99.2	2206		99.1						

TABLE IV-24

LO Linolenic PE Alkyd Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	15	117.8	0	15	120.4	0	5	100.0	0	5	100.0
0	20	107.8	0	20	113.4	0	10	96.5	0	10	98.0
0	30	101.9	0	30	104.6	0	15	94.2	0	15	98.6
0	45	100.0	0	45	101.5	0	20	93.8	0	20	98.6
1		100.2	1		101.0	0	30	93.9	0	30	97.5
1	30	102.5	2		100.4	0	45	93.9	0	45	96.4
2		104.5	3		100.3	1		92.9	1		95.6
2	30	105.7	5		100.0	1	30	92.6	1	15	94.2
3		105.7	21	30	101.0	2		92.6	1	30	95.4
4		105.6	45	30	111.5	2	30	91.1	2		95.9
5		105.6	71		112.0	3		91.4	2	30	94.7
6		105.7	165	30	112.4	4		91.1	3		95.0
23		106.2	237		112.3	4	30	91.4	4		94.9
49		106.5	334		112.7	6		92.0	5		93.6
76		106.7	525		112.9	22		88.7	6		92.8
167		107.4	742		112.8	46		88.6	22		92.5
215		108.4	1082		112.8				44	30	90.8
335		108.8	1440		112.7						
503		109.8	2184		111.9						
745		110.2									
1080		110.0									
1464		111.1									
2208		110.6									

TABLE IV-25

SO Oleic PE Alkyd Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	15	107.6	0	15	109.4	0	5	100.0	0	5	100.0
0	20	104.0	0	20	103.5	0	10	97.1	0	10	98.2
0	30	101.2	0	30	101.5	0	15	96.8	0	15	98.0
0	45	100.7	0	45	100.5	0	20	96.3	0	20	97.8
1		100.5	1		100.2	0	30	96.0	0	30	97.5
1	30	100.4	1	30	100.0	0	45	96.2	0	45	97.2
2		100.3	2		100.0	1		94.3	1		96.9
3		100.2	3	30	100.1	1	30	93.0	1	30	95.9
19		100.0	5		100.2	2		92.3	2		95.2
48		100.1	21		100.2	3	15	90.3	3		93.1
163		103.6	50		100.2	4		89.4	4		90.2
283		104.3	165	30	100.1	5		88.2	5		89.6
381		103.1	285		100.5	6		88.2	22		86.2
526		102.8	383		100.3	7		87.1	46		84.8
718		101.8	528		100.7	22		84.5			
1124		101.5	719		100.5	48		82.2			
1488		100.7	1128		101.3						
2232		99.7	1486		101.5						
			2184		101.6						

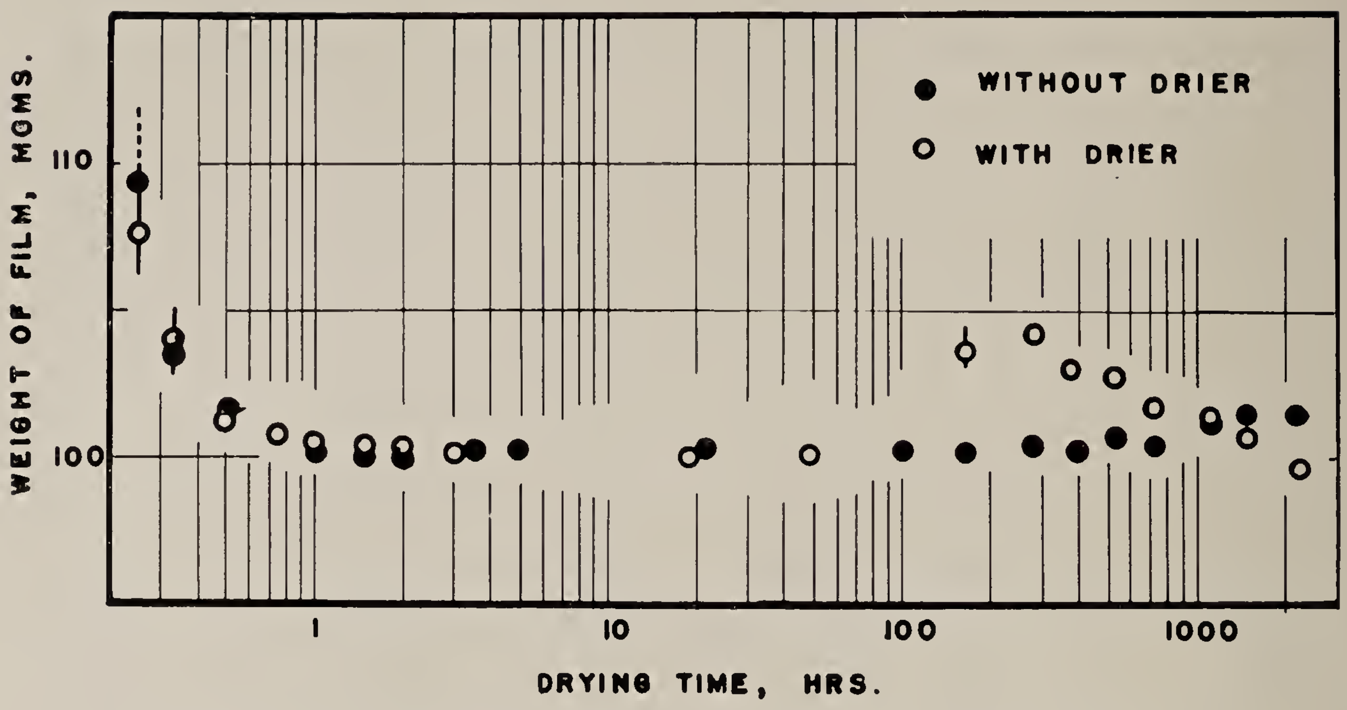


Fig. IV-18. SO oleic PE alkyd films: weight changes on air drying.

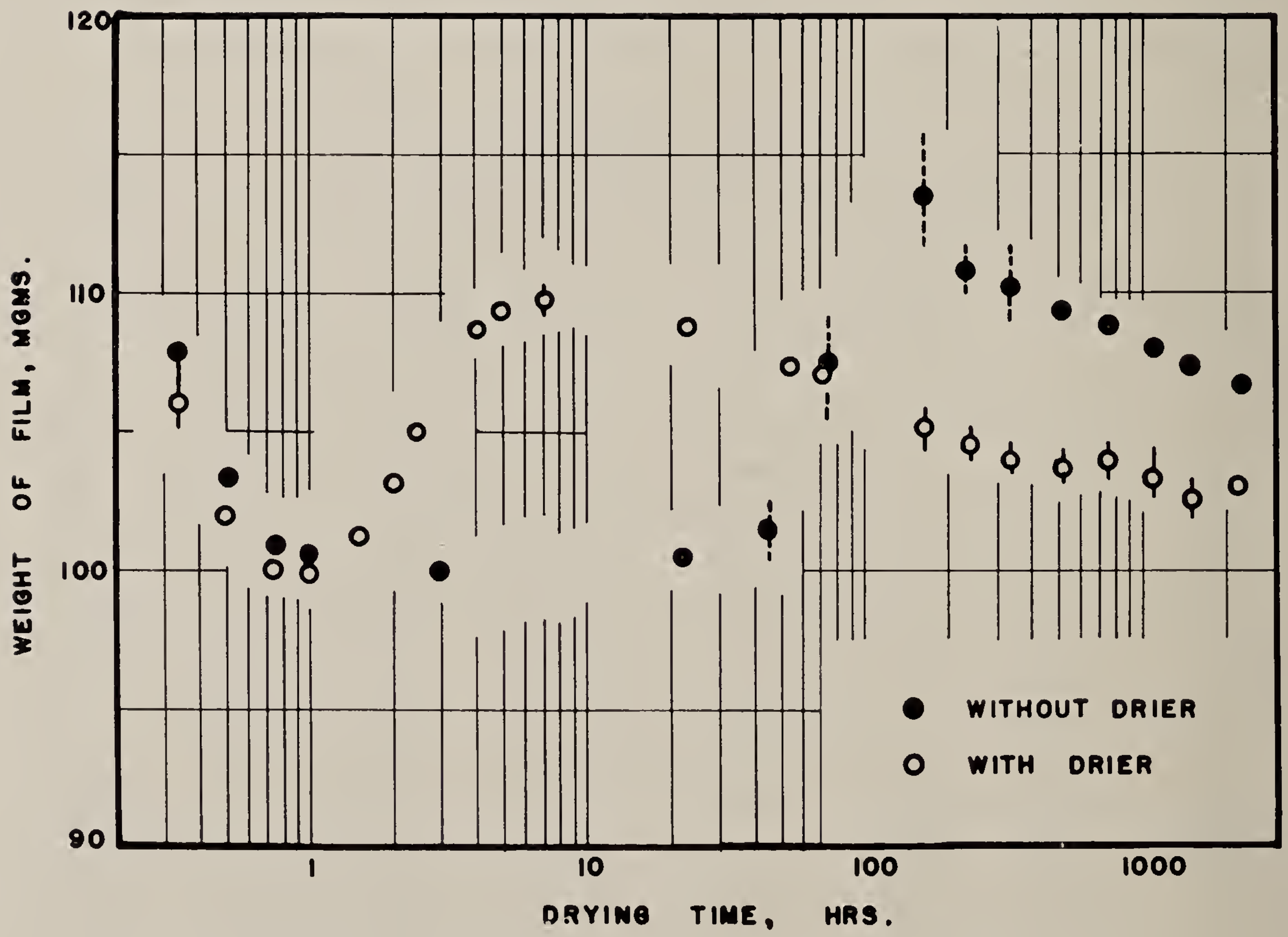


Fig. IV-19. Varnish linseed oil films: weight changes on air drying.

TABLE IV-26

Varnish Linseed Oil Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	20	106.1	0	20	107.9	0	5	100.0	0	5	100.0
0	30	102.0	0	30	103.4	0	10	97.0	0	7	99.3
0	45	100.1	0	45	101.0	0	15	95.8	0	10	99.3
1		100.0	1		100.7	0	20	94.7	0	15	100.5
1	30	101.3	3		100.0	0	30	94.2	0	20	101.6
2		103.2	22	30	100.4	0	45	93.0	0	30	100.0
2	30	105.0	45	30	101.5	1		92.1	0	45	98.2
4		108.7	74		107.5	1	30	91.2	1		96.8
7		109.7	163		113.5	2		90.6	2		97.6
23		108.8	235		110.8	3		89.6	5	30	96.7
71		107.2	336		110.3	4		90.2	22	30	92.3
167		105.1	504		109.5	23		82.2	45		88.7
335		104.0	1101		108.1	49		81.3			
748		104.0	1510		107.5	68		78.0			
1488		102.6	2208		106.8	94		79.2			
2231		103.2									

TABLE IV-27

Dehydrated Castor Oil Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	20	110.1	0	20	109.8	0	5	100.0	0	5	100.0
0	30	103.3	0	30	103.6	0	10	96.8	0	10	97.7
0	45	101.1	0	45	101.5	0	15	96.5	0	15	97.7
1		100.4	1		100.7	0	20	96.0	0	20	98.4
1	30	100.3	1	30	100.4	0	30	95.2	0	30	98.4
2		100.0	2		100.0	0	45	94.0	1		98.1
4		104.2	3		100.0	1		93.5	1	30	96.4
7		106.8	7		100.0	1	30	88.7	3		95.5
23		107.5	23		100.7	2		88.4	5		94.2
97		106.0	77		101.5	3		85.3	18	30	91.7
169		104.7	168		105.4	4		84.4	45	30	90.3
362		104.5	263		107.3	21		84.0	68	30	90.3
695		102.9	337		106.9	46		82.1	93		90.1
1128		102.0	720		105.9	117		79.5	164		88.7
2184		101.6	1680		105.1	215		75.0	261		85.8

TABLE IV-28

Commercial Alkyd Films: Progressive Changes in Weight on Drying

Air-dried						Baked					
With drier			Without drier			With drier			Without drier		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	15	114.8	0	20	105.3	0	5	100.0	0	5	100.0
0	20	107.6	0	30	101.4	0	10	96.8	0	10	98.4
0	30	102.1	0	45	100.3	0	15	95.9	0	15	98.3
0	45	100.5	1		100.0	0	20	95.9	0	20	98.2
1		100.3	1	30	100.0	0	25	95.2	0	30	98.1
1	36	100.0	2		100.0	1		94.6	0	45	97.2
3		103.6	4		100.0	2		93.5	1	30	96.1
20	30	103.4	5		100.0	3		92.3	2		94.8
92	30	102.9	6		100.1	4		91.4	3		94.8
164		102.5	29		100.2	5		90.4	4		94.8
358		102.3	53		100.5	6		89.7	21		90.7
524		101.5	72		100.5	23		84.5	45		89.3
691		100.9	167		104.2	47		83.3	69		89.2
1051		100.4	239		103.8	119		80.3	140		86.9
1485		100.4	338		103.0	215		77.4	239		84.5
2208		99.6	504		102.7						
			720		102.1						
			1080		101.5						
			1656		101.1						

TABLE IV-29

Progressive Changes in Weight on Drying of Films Cast after Aging with Drier; Films Air-dried (see page 48)

Trilinolenin			PE linoleate			PE linolenate			PE eleostearate		
Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.	Hr.	Min.	Wt.
0	15	100.0	0	15	104.6	0	15	106.6	0	10	114.5
0	30	100.0	0	30	100.2	0	30	100.0	0	20	100.4
0	45	101.1	0	45	100.0	0	45	100.1	0	30	100.0
1		102.5	1		100.2	1		101.4	0	45	100.0
1	15	103.6	1	30	101.0	1	15	102.8	1		100.0
2	15	106.4	2	15	102.4	2	15	106.4	1	30	100.4
3	45	106.9	3	24	105.0	2	45	106.9	2		100.5
5	45	106.8	5	30	107.1	4	15	106.9	3	25	100.7
7	45	106.8	6	15	107.3	5	15	106.9	4	40	100.7
8	45	106.8	8		107.4	7	15	106.8	6	30	100.8
23		106.6	23		105.5	25		107.1	24		100.5
31		106.5	55		103.7	102		107.4	31		100.5
54		106.5	120		100.9	170		107.7	50		100.1
72		106.4	200		99.3	266		107.9	97		99.1
122		106.4	295		97.3	338		107.9	169		97.9
168		106.2	481		96.2	504		107.7	267		96.7
264		106.0	698		95.3	768		107.2	336		96.0
697		104.1	1064		94.6	1297		106.5	506		95.6
1088		103.4	1488		94.0	1464		106.1	698		95.2
1418		103.2	2184		94.8	2208		106.3	1130		94.0
2210		102.5	4320		92.6	4200		104.8	1464		93.3
5040		101.3							2208		92.7

TABLE IV-30

Maximum Per Cent Gain in Weight of Films with and without Drier

Fatty acid component

Type vehicle	Oleic		Linoleic		Linolenic		Eleostearic	
	With drier	Without drier	With drier	Without drier	With drier	Without drier	With drier	Without drier
Glyceryl ester			12.5	15.00	11.00	19.20	0.40	10.5
PE ester			10.2	14.00	8.60	19.00	0.00	12.0
DiPE ester			10.5	15.00	10.5	17.80		
LO glycerol alkyd			3.2	7.00	6.5*	9.6	5.1	6.0
SO glycerol alkyd			4.0	5.5	4.6	7.0*		
LO PE alkyd	3.5	- -	8.0	9.00	11.1	13.00		
SO PE alkyd	5.0*	1.5*						

Control Vehicles

Linseed oil		Dehydrated castor oil		Commercial alkyd	
With drier	Without drier	With drier	Without drier	With drier	Without drier
10.00	12.5	7.5	7.5	4.0	4.2

- - Film not dry.

* Film still gaining weight after 100 days.

TABLE IV-31

Age in Hours of Film When Weight Reached Maximum, with and without Drier

Fatty acid component

Type vehicle	Oleic		Linoleic		Linolenic		Eleostearic	
	With drier	Without drier	With drier	Without drier	With drier	Without drier	With drier	Without drier
Glyceryl ester			15–20	100–125	3.5	45	6.0	25
PE ester	- -		6.5	125–150	300–350	55	4.0	75
DiPE ester	- -		10–15	140–145	400	50		
LO glycerol alkyd			500	80–90	2230*	1500	70	500
SO glycerol alkyd			100	160	1200	2200		
LO PE alkyd	100	- -	8.0	100	1500	520		
SO PE alkyd	220–250	2200*						

Control Vehicles

Linseed oil		Dehydrated castor oil		Commercial alkyd	
With drier	Without drier	With drier	Without drier	With drier	Without drier
10.0	165	24.0	250–300	4.0	125–150

- - Film not dry.

* Film still gaining weight after 100 days.

TABLE IV-32

Set-to-Touch Time (Hours), with and without Drier

	Fatty acid component							
	Oleic		Linoleic		Linolenic		Eleostearic	
Type vehicle	With drier	Without drier	With drier	Without drier	With drier	Without drier	With drier	Without drier
Glyceryl ester			15–20	100–120	3.0	40–45	0.5	1.5
PE ester	- -	- -	5.5	100	3.0	25	0.17	1.5
DiPE ester	- -	- -	5.5	120	1.5	35		
LO glycerol alkyd			3.5	70	0.75	40	0.25	1.5
SO glycerol alkyd			4.0	60	1.5	40–45		
LO PE alkyd	170	- -	4.0	100	4.0	40		
SO PE alkyd	0.25	0.25						

Control Vehicles

Linseed oil		Dehydrated castor oil		Commercial alkyd	
With drier	Without drier	With drier	Without drier	With drier	Without drier
4.0	150	3.0	170	1.0	100

- - Film not dry.

TABLE IV-33

Per Cent Loss in Weight of Film Baked 50 Hours, with and without Drier

	Fatty acid component							
	Oleic		Linoleic		Linolenic		Eleostearic	
Type vehicle	With drier	Without drier	With drier	Without drier	With drier	Without drier	With drier	Without drier
Glyceryl ester			20.0	23.0	13.0	15.5	16.0	9.5
PE ester	39.5	30.5	10.5	16.5	7.0	11.8*	9.2	6.0
DiPE ester	45.0	23.3	15.5	17.2	6.8	11.1*		
LO glycerol alkyd			16.5	10.0	40.0	18.0	15.0	15.0
SO glycerol alkyd			23.5	12.0	14.0	8.0		
LO PE alkyd	31.5	25.0	17.0	15.0	11.5	9.5		
SO PE alkyd	18.0	16.0						

Control Vehicles

Linseed oil		Dehydrated castor oil		Commercial alkyd	
With drier	Without drier	With drier	Without drier	With drier	Without drier
19.0	11.7	18.0	10.0	17.0	10.5

* Total % loss based on difference of % maximum and % minimum.

TABLE IV-34

Specific Gravity of Films, with and without Drier

Type vehicle	One week With drier	One week Without drier	One month With drier	One month Without drier	Three months With drier	Three months Without drier
Trilinolein	0.9101*	0.9769*	1.0796	0.9850	1.0995	1.0668
Trilinolenin	0.9689	1.0840*	1.1099	1.1011	1.0485	1.0345
Trieleostearin	0.8379	0.7830*	1.0429	1.1780	1.1797	1.1759
PE linoleate	1.0605	1.0155	1.0544	1.0742	1.0592	1.0673
PE linolenate	1.0823	1.0541		1.0694	1.1363	1.1244
PE eleostearate	1.0904	1.0866	1.0632	1.0194	1.0828	1.0840
DiPE linoleate	1.0593	1.0213	1.0441	0.9899	1.1086	1.1181
DiPE linolenate	1.0278	1.1108	1.1114	1.1581	1.1615	1.1881
LO linoleic glyc. alkyd	1.0805	0.9303	1.1723	1.0771	1.1211	1.1811
LO linolenic glyc. alkyd	1.1520	1.1299	1.0932	1.1501	1.2094	1.1970
LO eleostearic glycerol alkyd	1.1410	1.0794	1.1781	1.1012	1.0900	1.1368
SO linoleic glycerol alkyd	1.0844	1.1745	1.2115	1.1708	1.1415	1.1827
SO linolenic glycerol alkyd	--	1.1317†	1.3088	1.1702	1.2177	1.2310
LO linoleic PE alkyd	1.0456	1.0817	1.1323	1.1137	1.1584	1.1114
LO linolenic PE alkyd	1.0637	1.1131	1.1282	1.1851	1.1396	1.1568
SO oleic PE alkyd	‡	‡	1.1853	‡	‡	‡
Linseed oil	0.9944†	0.9700	0.9213†	0.9702	1.0707	1.0546
Dehydrated castor oil	1.0221	--	1.0200	--	1.0310	--
Commercial alkyd	1.0800	--	1.1638	1.1051	1.1423	1.1010

-- Film not dry.

* Value taken with water.

† Film dry at top, tacky at bottom.

‡ Film flaked when scraped.

TABLE IV-35

Comparison of Data of Two Laboratories (Scofield and Williams) on Gain in Weight and Setting Time of Films

Type vehicle	% Gain in weight Linoleic S.	% Gain in weight Linoleic W.	% Gain in weight Linolenic S.	% Gain in weight Linolenic W.	Set-to-touch time (hr.) Linoleic S.	Set-to-touch time (hr.) Linoleic W.	Set-to-touch time (hr.) Linolenic S.	Set-to-touch time (hr.) Linolenic W.
Glyceryl ester	12.7	12.5	17.8	11.0	9.2	15–20	5.2	3.0
PE ester	11.3	10.2	14.9	8.6	5.2	5.5	2.5	3.0
DiPE ester	12.8	10.5	13.3	14.9	4.4	5.5	1.9	1.5
LO glycerol alkyd	2.2	3.2	2.2	6.5	2.2	3.5	1.0	0.75
SO glycerol alkyd	1.7	4.0	1.0	4.6	3.5	4.0	1.5	1.5
LO PE alkyd	2.5	8.0	1.5	11.1	2.7	4.0	1.5	4.0

	Varnish linseed oil S.	Varnish linseed oil W.	Dehydrated castor oil S.	Dehydrated castor oil W.	Commercial alkyd S.	Commercial alkyd W.
% gain in weight	13.7	10.0				
Set-to-touch time (hr.)	4.7	4.0		3.0	3.3	1.0

products. The gain in weight is of course not a direct measure of oxygen absorbed; it is the balance between that absorption and the escape of volatile decomposition products (such as water, carbon dioxide, various aldehydes, and acids) which numerous investigators have described. If it were known—which it is not—what the rate of loss of these products is from the starting point, it would be possible to calculate the total amount of oxygen taken up by extrapolating the corrected gain in weight values to zero time.

The fact that baked films lost weight steadily from the start indicates that under oven conditions, volatile products lost exceed at all times the weight of added oxygen retained.

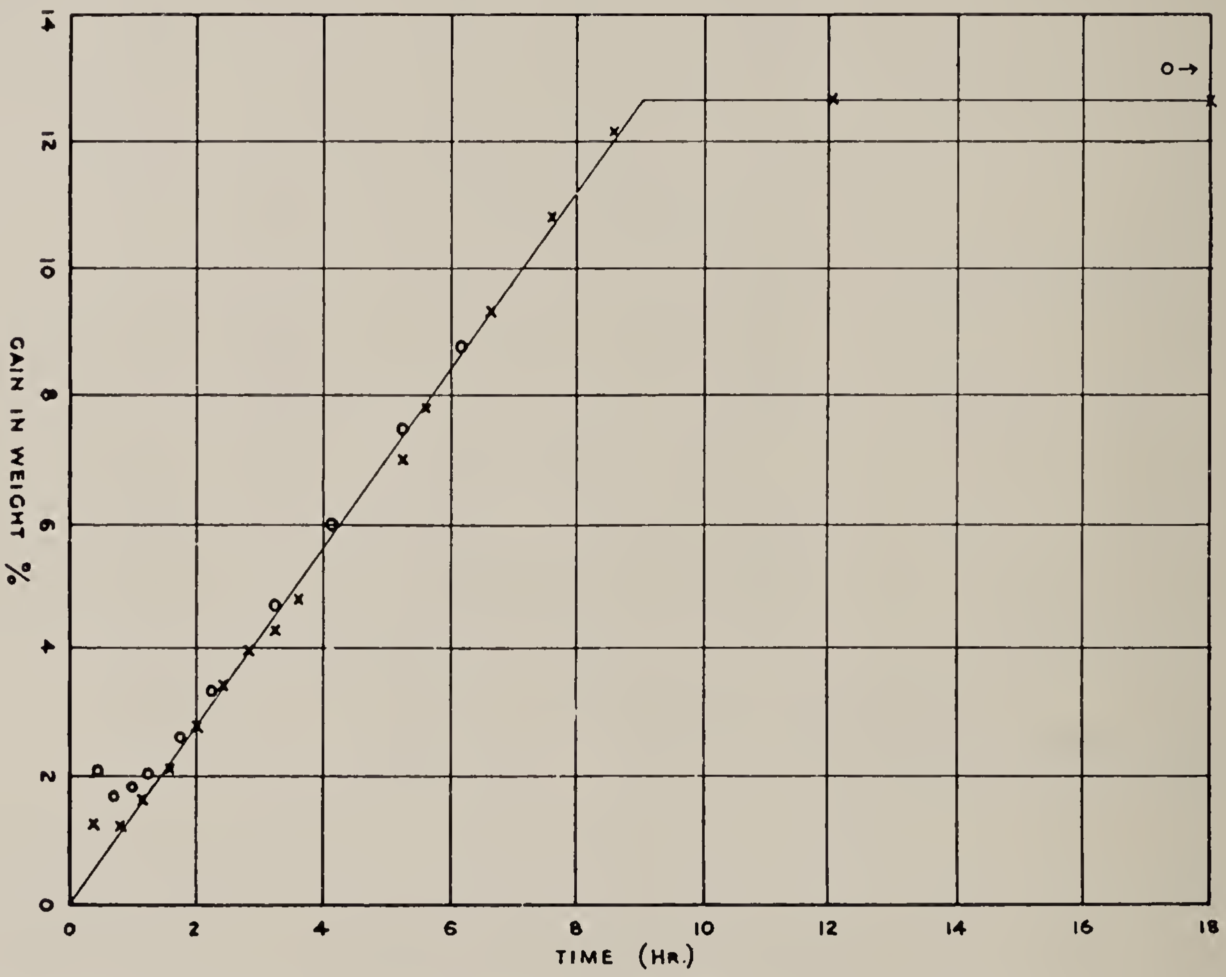


Fig. IV-20. Comparison of Scofield and Williams data on gain in weight of trilinolein.

On the whole, the synthetic compounds arrange themselves in about the expected order, and with about the expected differences due to their composition. Set-to-touch time is related directly to degree of unsaturation and to functionality; rate of oxygen absorption is related directly to degree of unsaturation. On the other hand, in the later stages of film drying, total oxygen absorption at a given time bears an inverse relationship to functionality, caused apparently by hindering effects of film gelling on solution and diffusion of oxygen into the film.

Ultimate Composition of Clear Films, Project 2—University of Louisville

This project, also carried out under Professor Williams' supervision at the University of Louisville (concurrently with Projects 3 and 5), measured the changes in carbon, hydrogen, and (by difference) oxygen content of films at various ages. Taken with the data of Project 1, it adds to our information about the amounts of oxygen compounds formed, retained, and lost in film drying.

Experimental

Experimental work on this project and Projects 3 and 5, extending over a period of four years, was performed by I. N. Cooperman, M. M. Moudgill, M. L. Johnson, and S. Y. Yuan. A partial report (3) was given at the Federation meeting in November, 1950. They determined the composition of film samples by combustion in a semimicro train using the general procedure of Natelson, Brodie, and Conner (1), slightly modified to accommodate the films.

They used a fused quartz combustion tube 36 inches long and $1^1/_8$ inches inside diameter, placed in two Heavy Duty sectional tube furnaces, the primary held at 550° to 600° C. and the secondary at 200°. The packing in 13 inches of the secondary furnace was lead peroxide on glass wool. In the primary furnace were 7 inches of copper oxide and 6 inches of mixed copper oxide and fused lead chromate lumps. The initial 9 inches was left free for the combustion boat and a copper oxide coil. Oxygen from a commercial cylinder passed at constant low pressure through a preheater packed with mixed lead chromate and copper oxide, a sulfuric acid bubble counter, a soda lime and phosphorus pentoxide scrubber, the combustion tube, two drierite tubes, an ascarite tube, and finally a moisture stopper packed with drierite and soda lime.

When the furnaces had reached desired temperatures, the preheater was heated to 550° C., and the system was flushed for 45 minutes at a rate of 80 to 90 bubbles of oxygen per minute. The absorption tubes were weighed and inserted in position. About 100 mg. of film sample was weighed into the combustion boat which was put into the tube, and oxygen passed at the rate noted. The portion of the tube containing the boat was heated slowly by a gas flame, then at 650° C. for 2 hours. Some of the more easily oxidizable samples, when heated too fast, exploded, blowing out the rubber stopper at the end of the tube. A 30-minute purge period followed, after which ascarite and drierite absorption tubes were weighed and carbon and hydrogen were calculated. If the C:H ratio found in any run was markedly inconsistent with earlier and later runs, the data for the run were discarded. An assortment of films cured under the conditions of the test was weighed before and after desiccation for 2 hours over phosphorus pentoxide and found to carry an average of 3% absorbed moisture; all combustion data were therefore corrected by this amount.

Three of the films analyzed in this project were prepared before the standard conditions were finally prescribed, and before the cobalt-lead drier solution was distributed. For these compounds (trilinolein and PE and diPE linoleates), the mixing procedure was as follows: 4 or 5 drops of a solution of lead naphthenate were weighed into a tared 25-ml. pyrex Florence flask, and enough of the synthetic oil added (3 to 5 grams) to bring the percentage of lead (as metal) to 0.5, by weight, of the compound; the mixture was thoroughly stirred and was held under vacuum for 48 hours before laying the film.

After the Federation drier was received, the standard procedures were followed, except as otherwise noted. Ampules as received were placed in a graduated cylinder fitted with rubber stopper and glass stopcock. The weight and volume of the compound, as marked, were noted, and mineral spirits or other solvent added to obtain proper viscosity. The drier was also added at the rate of 0.3 ml. to 3 grams of nonvolatile compound, and aged under vacuum as directed.

The experimenters tried various techniques for laying films and finally adopted the one they found most satisfactory, the same one used later in the Louisville series of Project 1: withdrawal of a calculated volume from the sample vial, ejection onto the glass plate, and brushing out to a uniform film over a fixed area. Crawling, where it occurred, was corrected by brushing or spreading with a clean dry finger tip. Standard conditions were observed in drying the films. Portions for analysis were scraped from the plates by a clean razor blade with a perfect cutting edge, to assure complete removal.

Peculiarities of some of the films were noted as follows. Trilinolenin crawled, and when finally restored to a continuous film, it dried tack-free in 24 hours to a greenish yellow wrinkled film, which rapidly embrittled with age.

Trieleostearin dried to a film with a crow's-foot pattern of wrinkling. PE oleate did not become dry or even tack-free after 630 days; it could not be analyzed satisfactorily. DiPE oleate crawled and could not be leveled; after two months it started to become tacky. The analytical results, which are of doubtful value, were as follows:

Film age (days)	% C (Theoretical = 77.6)	% H (Theoretical = 10.8)	% O (Theoretical = 11.6)	C:H ratio
78	66.2	9.3	24.5	7.2
165	64.8	8.8	26.4	7.4
331	63.2	11.3	25.5	5.6
332	63.5	11.0	25.5	5.8

These figures indicate, surprisingly, a greater loss of carbon than of hydrogen, perhaps pointing toward a build-up of water in the film.

LO linolenic glycerol alkyd thickened rapidly on exposure to air, and was hard to lay smooth. Several films showed frost spots. The corresponding eleostearic alkyd was even more viscous. The SO eleostearic glycerol alkyd had gelled before opening of the ampule, making it impossible to obtain valid results. LO oleic PE alkyd dried to a tacky state in about two months and gave the following analyses, the significance of which is limited:

Film age (days)	% C	% H	% O
64	70.0	10.1	19.9
72	67.0	12.1	20.9
236	62.9	8.7	28.4
445	65.6	7.2	27.2

SO oleic PE alkyd, though viscous even after thinning with diisobutyl ketone, brushed out easily and dried to an extremely brittle film, which for the first 6 days flew into minute snowy flakes at the touch of the razor blade.

The commercial alkyd gave trouble with crawling, and like some of the pure alkyds dried so hard that it was difficult to remove from the glass.

The analytical results are shown in detail in Tables IV-36 to IV-55. They were plotted in Figs. 1 to 15 on pages 1022 to 1026 of No. 311 of the *Official Digest.* The curves, which exhibit the sharp initial rise in oxygen percentages, leveling off to almost constant values for all the compounds studied, are so similar that only one, Fig. IV-21 (trilinolenin), is reproduced here.

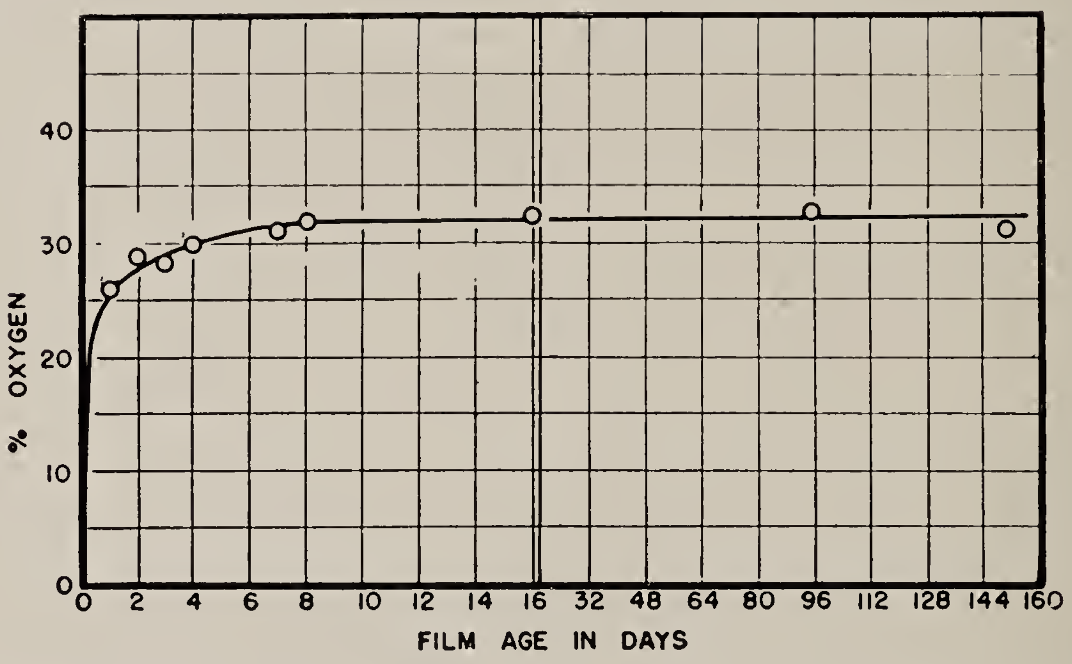


Fig. IV-21. Changes in oxygen content of drying trilinolenin films.

Discussion

The method of analyzing for carbon and hydrogen by combustion and determining oxygen by difference incorporates the errors of both the carbon and hydrogen determinations in the reported oxygen content. The results for oxygen content are therefore more scattered than might be wished. Most of the materials, however, seemed to reach a relatively stationary condition after several days. Averages of measured values after that time, therefore, appear to be relatively accurate. They are shown for the linoleic and linolenic esters in Table IV-56. Also given in this table are figures for the calculated theoretical maximum oxygen content of the film, assuming that the gain in weight shown by the films in drying is a direct measure of

Tables IV-36 to IV-56 follow.
Text continues on page 91.

TABLE IV-36
Combustion Analysis of Trilinolein Films
(Drier: 0.5% Pb as lead naphthenate by weight)

Film age (days)	% C	% H	% O	Atoms O/mole of compound
1	63.4	11.8	24.8	16.1
2	59.4	10.6	30.0	21.0
4	60.8	10.0	29.2	20.1
7	62.9	10.0	27.1	18.2
14	63.1	9.3	26.8	17.9
51	58.4	9.3	32.3	25.3
170	63.1	7.9	29.0	19.9
587	59.5	10.1	30.4	21.4

TABLE IV-37
Combustion Analysis of Trilinolenin Films

Film age (days)	% C	% H	% O	Atoms O/mole of compound
1	65.5	8.5	26.0	17.1
2	63.0	8.1	28.9	19.7
3	63.2	8.4	28.4	19.3
4	62.2	7.9	29.9	20.7
7	61.4	7.4	31.2	22.0
8	61.3	6.9	31.8	22.6
16	61.1	6.4	32.5	23.4
95	60.3	6.9	32.8	23.7
149	61.5	7.1	31.4	22.4
214	61.2	8.8	30.0	21.0
582	60.5	7.0	32.5	23.6

TABLE IV-38
Combustion Analysis of Trieleostearin Films

Film age (days)	% C	% H	% O	Atoms O/mole of compound
(3 hr.)	70.5	9.3	20.2	
1	70.4, 66.2	10.2, 8.0	19.4, 25.8	11.7, 16.9
2	64.3	8.4	27.3	18.3
3	65.3	8.1	26.6	17.6
4	62.4	8.3	29.3	20.1
7	63.7	6.9	29.4	20.2
10	61.2	6.4	32.4	23.3
11	63.3	6.8	29.9	20.7
14	63.4	8.4	28.2	19.1
21	63.7	6.8	29.5	20.3
29	64.2	8.6	27.2	18.2
50	61.6	8.6	27.2	20.6
51	62.1	7.3	30.6	21.4
222	58.7	9.8	31.5	22.3
223	57.7	9.3	33.0	23.9

TABLE IV-39
Combustion Analysis of PE Linoleate Films
(Drier: 0.5% Pb as lead naphthenate by weight)

Film age (days)	% C	% H	% O	Atoms O/mole of compound
1	73.5, 78.3, 72.3	9.6, 10.6, 12.2	16.9, 11.2, 15.5	12.6, 7.9, 11.4
2	68.0	9.0	23.0	16.6
3	67.9	9.0	23.5	19.1
4	67.0	9.2	23.8	19.4
5	67.3	9.0	23.7	19.3
7	65.5, 63.7	8.8, 10.0	25.8, 26.3	21.7, 22.2
14	65.8, 66.2	9.6, 8.4	24.6, 25.4	20.3, 21.2
28	64.2	9.4	26.4	22.4
31	65.3	9.0	25.7	21.5
48	63.3	8.9	27.8	24.0
112	64.6	8.4	27.0	23.0
476	63.3	8.4	28.3	24.6

TABLE IV-40

Combustion Analysis of PE Linolenate Films

Film age (days)	% C	% H	% O	Atoms O/mole of compound
1	64.0	9.5	26.5	22.3
2	64.6	9.4	26.0	22.7
3	65.0	9.1	25.9	21.6
4	65.8	9.4	24.8	20.4
7	65.5	9.9	24.6	20.3
15	66.8	9.9	23.3	18.8
21	62.8	9.3	27.9	23.9
32	65.5	6.8	27.7	23.6
183	65.8	8.6	25.6	21.2
360	63.9	8.3	27.8	23.8
561	60.3	10.1	29.6	26.0
566	59.1	10.5	30.4	27.0

TABLE IV-41

Combustion Analysis of PE Eleostearate Films

Film age (days)	% C	% H	% O	Atoms O/mole of compound
(3 hr.)	71.7	8.8	19.5	
1	67.0	8.8	24.2	19.7
2	66.9, 66.6	9.3, 9.0	23.8, 24.4	20.0,—
3	66.0	10.2	23.8	19.3
6	64.3	8.4	27.3	24.6
9	63.6	7.9	28.5	24.6
17	61.9	7.0	31.1	27.9
24	61.9	8.1	30.0	26.5
42	60.6	8.6	30.8	27.5
157	59.8	10.7	29.5	25.8
379	59.7	9.5	30.8	27.5

TABLE IV-42
Combustion Analysis of DiPE Linoleate Films
(Drier: 0.5% Pb as lead naphthenate by weight)

Film age (days)	% C	% H	% O	Atoms O/mole of compound
1	66.1	9.7	24.2	32.0
2	70.0	10.3	19.7	24.4
4	67.8	9.3	22.9	29.6
9	65.5	9.1	25.4	34.0
21	65.3	9.4	25.3	33.8
58	62.8	9.8	27.4	37.6
63	64.0	10.0	26.0	35.0
492	61.9	8.0	30.1	42.9
829	63.1	9.8	27.1	37.1

TABLE IV-43
Combustion Analysis of DiPE Linolenate Films

Film age (days)	% C	% H	% O	Atoms O/mole of compound
1	68.9, 68.8	10.1, 10.1	21.0, 21.1	26.4, 26.6
2	70.0, 65.0, 67.0	10.4, 9.3, 9.4	19.6, 25.7, 23.6	24.2, 34.2, 30.7
4	70.0	10.7	19.3	23.8
7	64.0	9.4	26.6	36.0
23	63.8	9.0	27.2	37.0
184	62.4	7.1	30.5	43.4
189	61.4	8.2	30.4	43.2
377	62.6	7.2	30.2	42.8
527	62.4	10.3	27.3	37.2

TABLE IV-44

Combustion Analysis of LO Linoleic Glycerol Alkyd Films

Film age (days)	% C	% H	% O	Atoms O/mole of compound
(4 hr.)	64.1	7.0	28.9	
1	64.1	6.3	29.6	14.6
2	61.7	7.1	31.2	15.8
3	62.6	6.9	30.5	15.3
4	63.6	6.5	29.9	14.6
5	62.5	7.0	30.5	15.3
7	61.2	7.1	31.7	16.2
13	62.5	7.2	30.3	15.1
20	61.8	6.9	31.3	15.8
28	59.3	6.3	34.4	18.2
40	61.7	6.8	31.5	16.0
87	63.5	6.9	29.6	14.6
113	63.5	6.2	30.3	15.1
236	57.6	10.2	32.2	16.5
237	58.3	8.2	33.5	17.5

TABLE IV-45

Combustion Analysis of LO Linolenic Glycerol Alkyd Films

Film age (days)	% C	% H	% O	Atoms O/mole of compound
(3 hr.)	68.4	8.0	23.6	
1	66.6	7.2	26.2	12.3
2	65.8	7.3	26.9	12.7
3	67.7	7.3	25.0	11.5
4	65.7	7.5	26.8	12.7
7	66.3	6.9	26.8	12.7
11	65.3	7.5	27.2	12.9
15	64.0	6.9	29.1	14.2
25	60.6	6.5	32.9	16.9
35	63.2	7.2	29.6	14.5
114	63.1	6.8	30.1	14.9
239	58.5	10.7	30.8	15.4

TABLE IV-46
Combustion Analysis of LO Eleostearic Glycerol Alkyd Films

Film age (days)	% C	% H	% O	Atoms O/mole of compound
(3 hr.)	70.4	7.8	21.8	
1	68.1	8.0	23.9	10.9
2	64.7	7.4	27.9	13.4
3	67.0	8.1	24.9	11.5
4	64.1	7.3	28.6	13.9
6	65.3	7.3	27.4	13.0
7	64.6	7.4	28.0	13.4
11	63.5	7.1	29.4	14.4
14	62.9	7.6	29.5	14.5
17	64.4	7.6	28.0	13.4
23	64.1	7.7	28.2	13.6
29	63.2	7.2	29.6	14.6
62	65.2	7.7	27.1	12.9
86	63.6	7.0	29.4	14.4

TABLE IV-47
Combustion Analysis of SO Linoleic Glycerol Alkyd Films

Film age (days)	% C	% H	% O	Atoms O/mole of compound
1	60.2, 62.0	8.9, 8.9	30.9, 29.1	13.8, 12.8
3	60.6	8.0	31.4	14.2
4	60.8	7.5	31.7	14.4
5	60.9	8.0	31.1	14.0
6	60.2	8.1	31.7	14.4
7	58.9	8.5	32.6	15.1
10	60.0	8.1	31.9	14.6
14	58.5	9.1	32.4	14.9
25	61.5	6.3	32.2	14.8
36	61.0	9.4	30.6	13.7
44	61.5	7.0	31.5	14.3
54	60.0	9.9	30.1	13.4
66	59.8	8.6	31.6	14.4
170	58.8	8.6	32.6	15.1

TABLE IV-48

Combustion Analysis of SO Linolenic Glycerol Alkyd Films

Film age (days)	% C	% H	% O	Atoms O/mole of compound
1	67.5	9.6	22.9	9.2
2	66.7	6.3	27.0	11.4
3	69.1	9.2	21.7	8.6
4	67.2	7.0	25.8	10.8
5	67.7	7.8	24.5	10.0
6	66.1	8.1	25.8	10.8
7	64.7	7.4	27.9	12.0
12	67.4	7.1	25.5	10.6
13	66.6	6.2	27.2	11.6
25	65.9	7.8	26.3	11.0
32	64.4	6.7	28.9	12.6
165	61.9	9.0	29.1	12.7

TABLE IV-49

Combustion Analysis of SO Eleostearic Glycerol Alkyd Films

Film age (days)	% C	% H	% O	Atoms O/mole of compound
1	66.0	8.4	25.6	10.6
2	64.2	6.0	29.8	13.1
4	66.5	7.0	26.5	11.1
7	66.1	7.9	26.0	10.9
15	63.9	6.8	29.3	12.8
30	63.6	7.6	28.8	12.5
51	65.9	6.5	27.6	11.8
403	60.2	9.8	30.0	13.2

TABLE IV-50

Combustion Analysis of LO Linoleic PE Alkyd Films

Film age (days)	% C	% H	% O	Atoms O/mole of compound
1	65.4	7.3	27.3	19.2
2	63.0	7.5	29.5	21.4
4	64.7	7.7	27.6	19.5
6	63.4	7.5	29.1	21.0
11	63.5	7.6	28.9	20.8
14	63.1	7.7	29.2	21.1
54	62.4	7.4	30.2	22.1
63	62.9	8.3	28.8	20.6
134	64.4	8.2	27.4	19.3
480	62.9	8.0	29.1	21.0

TABLE IV-51

Combustion Analysis of LO Linolenic PE Alkyd Films

Film age (days)	% C	% H	% O	Atoms O/mole of compound
1	68.3, 68.0	8.8, 8.0	22.9, 24.0	15.0, 16.0
2	67.8, 67.2, 69.3	8.2, 7.9, 8.5	24.0, 24.9, 22.2	16.0, 16.8, 14.5
3	66.0, 66.9	7.5, 8.1	26.5, 25.0	18.3, 16.9
4	68.2, 67.5	8.0, 8.1	23.8, 24.4	15.8, 16.4
8	67.9	8.2	23.9	15.9
15	66.2, 65.0	8.0, 7.4	25.8, 27.6	17.7, 19.3
16	64.2	7.1	28.7	20.4
17	63.7	7.4	28.9	20.6
71	62.3	6.3	31.4	23.2
142	63.4	7.7	28.9	20.6
489	63.3	7.9	28.8	20.6

TABLE IV-52
Combustion Analysis of SO Oleic PE Alkyd Films

Film age (days)	% C	% H	% O	Atoms O/mole of compound
1	64.0, 63.5	10.1, 10.1	25.9, 26.4	14.8, 14.6
2	61.3	10.3	28.4	16.4
3	63.5	7.0	29.5	17.2
5	64.0	7.3	28.7	16.6
6	63.6	7.8	28.6	16.5
7	63.0	8.2	28.8	16.7
9	58.7	7.2	34.1	21.2
15	62.1	8.1	29.8	17.5
20	60.6	8.7	30.7	18.3
24	56.0	13.1	30.9	18.4
38	59.0	7.2	33.8	21.0
52	60.5	8.6	31.9	19.3
64	60.0	8.2	31.8	19.2

TABLE IV-53
Combustion Analysis of Varnish Linseed Oil Films

Film age (days)	% C	% H	% O
1	62.1, 61.9	9.6, 10.9	28.3, 27.2
2	59.6	9.5	31.3
3	60.2	10.1	29.7
4	59.3	10.1	30.6
5	59.2	10.3	30.5
6	59.8	8.3	31.9
7	58.8	9.0	32.2
8	60.6	8.0	31.4
9	61.1	8.4	30.5
11	59.8	8.9	31.3
15	60.0	9.9	30.1
16	60.0	9.4	30.6
21	59.4	10.3	30.3
28	60.2	9.7	30.1
35	59.2	9.5	31.3
53	60.2	9.6	30.2
55	60.6	8.2	31.2
65	60.5	8.7	31.8

TABLE IV-54

Combustion Analysis of Dehydrated Castor Oil Films

Film age (days)	% C	% H	% O
1	62.0, 61.5	9.7, 9.5	28.3, 29.0
2	60.1	9.2	30.7
4	60.7	9.1	30.2
5	58.8	10.6	30.6
6	61.2	9.2	29.6
8	60.0	9.0	31.0
9	61.1	9.8	29.1
14	58.0	10.1	31.9
21	60.7	11.1	28.2
30	61.5	9.8	28.7
35	61.9	9.5	28.6
45	61.1	10.3	28.6
56	59.5	10.4	30.1
65	58.5	10.0	31.5

TABLE IV-55

Combustion Analysis of Commercial Alkyd Films

Film age (days)	% C	% H	% O
1	58.0, 57.7	10.4, 11.0	31.6, 31.3
2	57.9	10.1	32.0
3	56.0	10.4	33.6
4	57.1	10.0	32.9
5	57.4	10.1	32.5
6	55.5	11.1	33.4
8	56.8	10.3	32.9
10	56.2	10.7	33.1
15	57.1	10.2	32.7
22	56.6	10.8	32.6
32	56.2	10.0	33.8
43	56.6	10.2	33.2
52	56.5	10.5	33.0
64	57.0	9.9	33.1

TABLE IV-56

Oxygen Content of Dried Films as Determined and as Calculated from Gain in Weight

Compound	Determined (Williams)	Calculated	
		Williams	Scofield
Trilinolein	29.26	20.8	21.0
PE linoleate	25.48	19.0	19.8
DiPE linoleate	26.89	19.8	21.4
Trilinolenin	30.94	19.8	24.4
PE linolenate	26.68	17.9	22.4
DiPE linolenate	28.71	22.9	21.8

oxygen absorbed and using the total gains from the work of both Williams and Scofield on Project 1.

It is at once apparent that the actual proportion of oxygen in the dried films is substantially higher than would be arrived at by the direct absorption of oxygen in the amount measured by the gain in weight. Moreover, there has been a decrease in the proportions of both carbon and hydrogen. Obviously, then, there has been a loss of both carbon and hydrogen from the films, presumably in the form of carbon dioxide, water, and low molecular weight organic compounds. The possibility that free hydrogen and hydrocarbons are formed is not excluded, although not necessarily required by the foregoing observations.

Quantitatively, these results are decidedly different from those found in the bulk oxidation of oils. All the evidence from these two projects indicates that oxygen absorption by a drying film is not a simple matter and that the products formed may differ qualitatively as well as quantitatively under different drying conditions.

In the evaluation of Project 2 data by Williams and Long, they note that strict comparability of analyses made at varying lengths of time after the laying of the film is precluded by the fact that gain in weight due to oxygen absorption and loss due to volatilization of scission products proceed simultaneously at unknown rates. They assume, however, that these scission products are chiefly carbon dioxide and water, each of which contains high proportions of oxygen; and that therefore the losses of oxygen-free compounds (i.e., carbon plus hydrogen) would be low. Since the composition of the starting compound is known, oxygen gain can be found on the basis of number of atoms of oxygen per mole of monomeric substance as calculated from the C plus H total in that monomeric form. The calculated maximum error in this procedure is 3.4%, with a probable value of about 1%. They present in Table IV-57 certain arbitrary theoretical values for oxygen gained per mole of oil at saturation, based on the assumption that 1 mole of oxygen is added for each double bond. Admittedly, since oxygen does not actually saturate the double bonds, this assumption is very limited in its validity. It simply makes allowance for the experimentally observed fact that in the early life of films the total amount of oxygen added bears some relation to the total number of double bonds present. In the tables (IV-36 to IV-55) of experimental data, the total number, at each age, of atoms of oxygen per mole of original oil are shown, calculated as in the following examples; and these values are plotted in Figs. IV-22 to IV-27.

Example 1. Simple ester (Trilinolein, mol. wt. 878.8): combustion analysis at 1 day film age, 63.4% C, 11.8% H, 24.8% O; C + H, 75.2%. C + H content per mole of oil, 782 grams.

Atoms of oxygen per mole of oil: (24.8/75.2) × (782/16) = 16.1.

Example 2. Alkyd (LO linoleic glycerol alkyd, oil length 60.5%): combustion analysis at 1 day film age, 64.1% C, 6.3% H, 29.6% O; C + H, 70.4%.

Alkyd composition:	% by wt.	Mol. wt.	Mole fraction
Trilinolein	60.5	878.8	0.483
Glyceryl triphthalate	39.5	536.0	0.517

Molecular weight of alkyd, oxygen-free basis:

	Grams C + H/mole of oil		Mole fraction in alkyd		
Trilinolein	782	×	0.483	=	378
Glyceryl triphthalate	344	×	0.517	=	178
C + H content per mole of alkyd				=	556 grams

Atoms of oxygen per mole of alkyd: (29.6/70.4) × (556/16) = 14.6.

Determination of arbitrary theoretical oxygen content at saturation in atoms per mole:

Example 1. Trilinolein, with 6 atoms of oxygen originally, has 6 double bonds and can add 12 atoms of oxygen, making 18.

Example 2. LO linoleic glycerol alkyd:

	Mole fraction in alkyd	Atoms O/mole of formula	Atoms O in alkyd
Trilinolein	0.483	18	8.69
Glyceryl triphthalate	0.517	12	6.20
			14.89

As the tables show, the experimental values of oxygen content exceed the theoretical values for trilinolein, PE linoleate, LO and SO linoleic glycerol alkyds, and SO oleic PE alkyd. Most of the other compounds showed values which approached these arbitrarily calculated values, but those for linolenates and eleostearates of PE and diPE, and for all the other alkyds, were appreciably below them. The higher values for eleostearates than for linolenates are somewhat puzzling because the data from other projects (notably Project 24, Chapter XIII) indicate that eleostearate films set at lower levels of oxygen absorption and lower peroxide values than linolenates,

TABLE IV-57

Oxygen Content of Original Compounds (Atoms per Mole of Compound) vs. Assumed Content at Saturation

Column *A:* Atoms per mole of original compound.

Column *B:* Atoms per mole at assumed complete saturation.

	Fatty acid component							
	Oleic		Linoleic		Linolenic		Eleostearic	
Compound	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Glyceryl ester			6	18	6	24	6	24
PE ester			8	24	8	32	8	32
DiPE ester			13	37	13	49		
LO glycerol alkyd			9.11	14.89	9.10	17.80	9.10	17.80
SO glycerol alkyd			9.90	14.10	9.91	16.16	9.91	16.16
LO PE alkyd			10.75	21.27	10.73	27.59		
SO PE alkyd	14.15	16.00						

after which the further addition of oxygen is greatly hindered. That the linoleates and linolenates differ only slightly is not unexpected; the third double bond of linolenates is somewhat superfluous insofar as oxidative polymerization is concerned, and once the linolenate films have set it would be expected that their additional unsaturation would be attacked by oxygen only slowly. The departures of the observed from the theoretical values serve to show that in films, to an even greater extent than in bulk, the oxygen content of drying oils is governed by secondary factors. Among these is the formation of a skin on the surface of the film which strongly influences the diffusion and convection of oxygen in the increasingly viscous underlying layers.

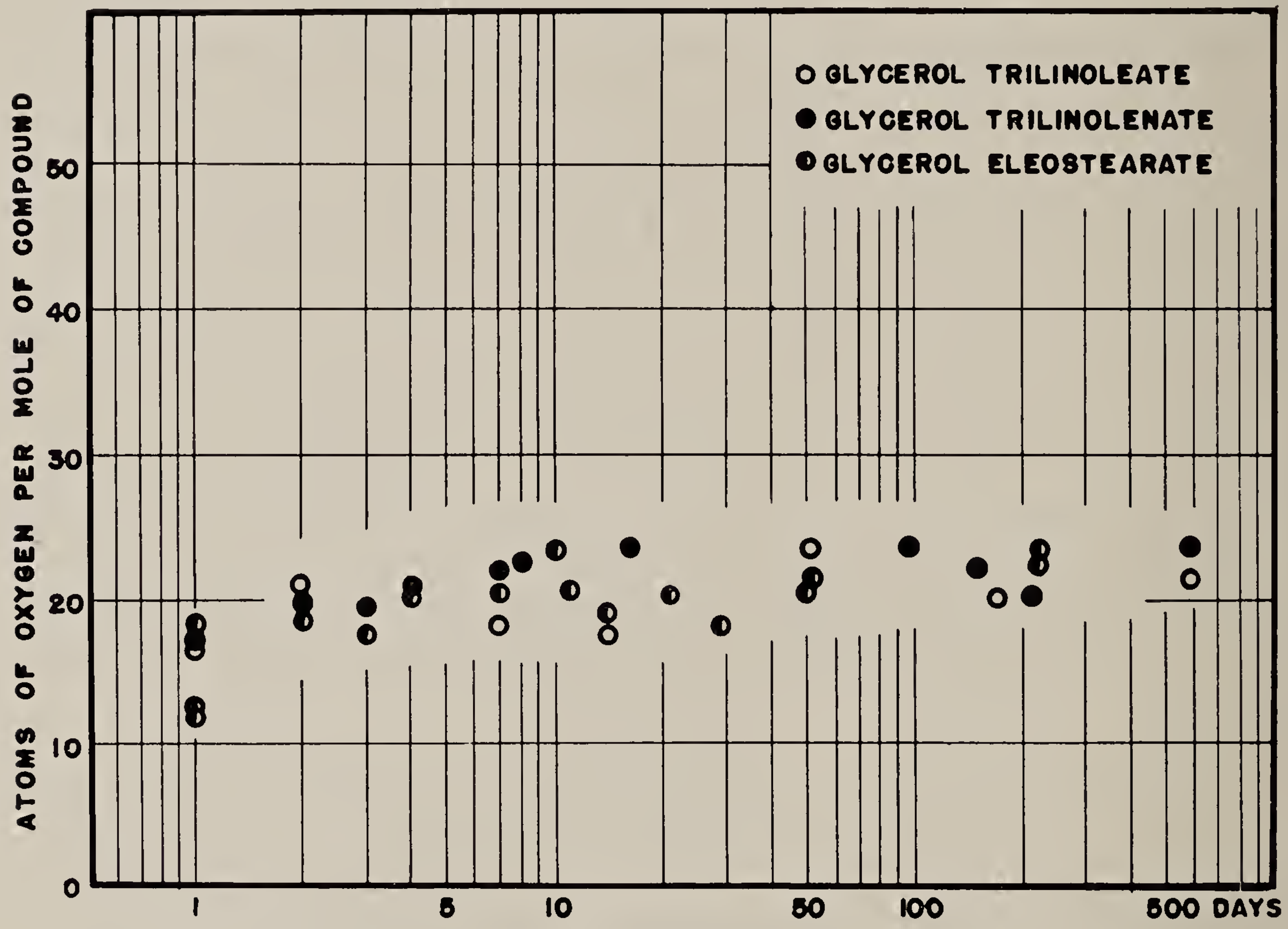


Fig. IV-22. Oxygen content of drying films of glycerol esters.

Loss of Solubility of Films on Aging, Project 3—University of Louisville

As drying oil films convert from liquids to solids and gradually harden, they become less soluble in organic solvents. The objective

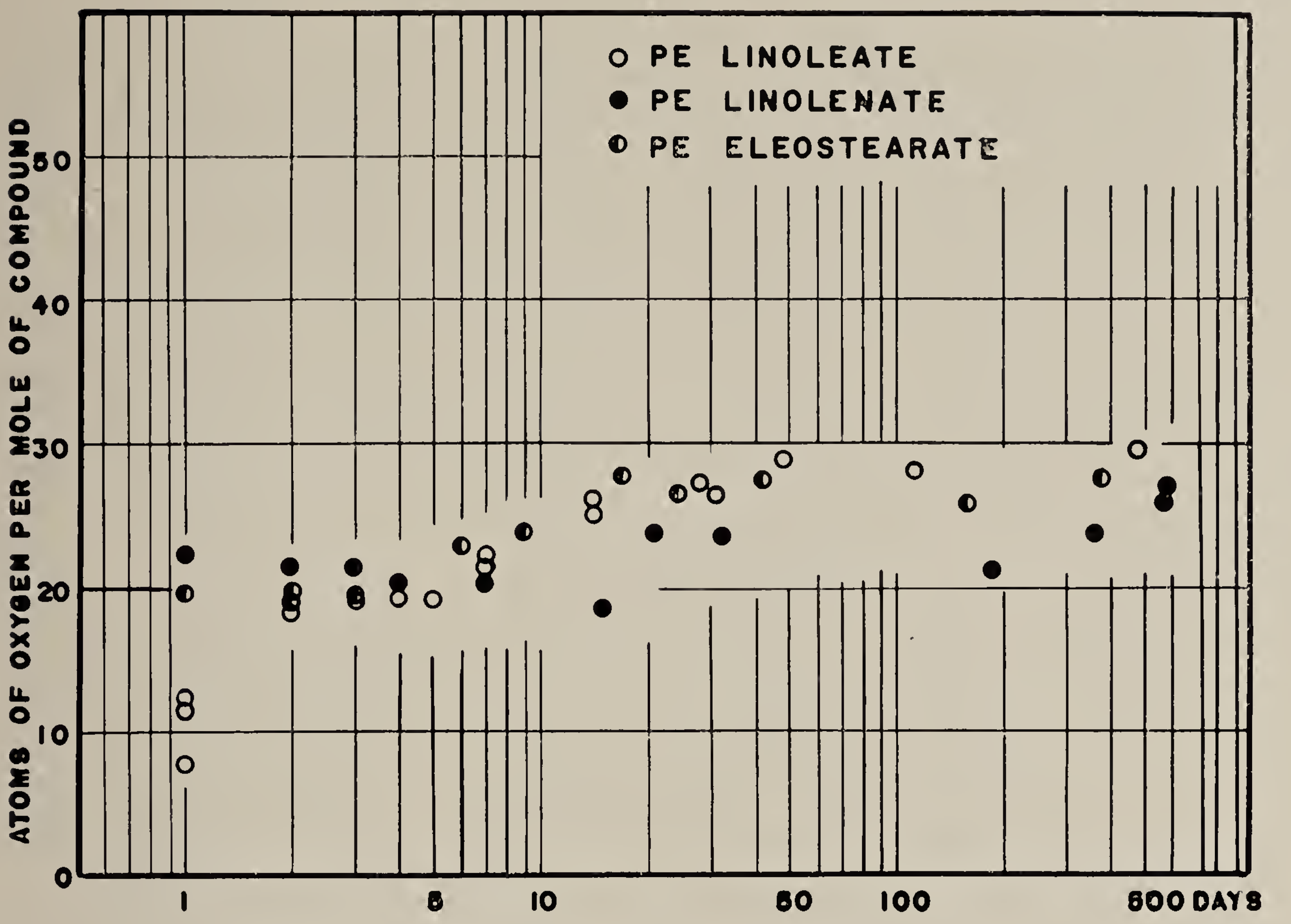


Fig. IV-23. Oxygen content of drying films of PE esters.

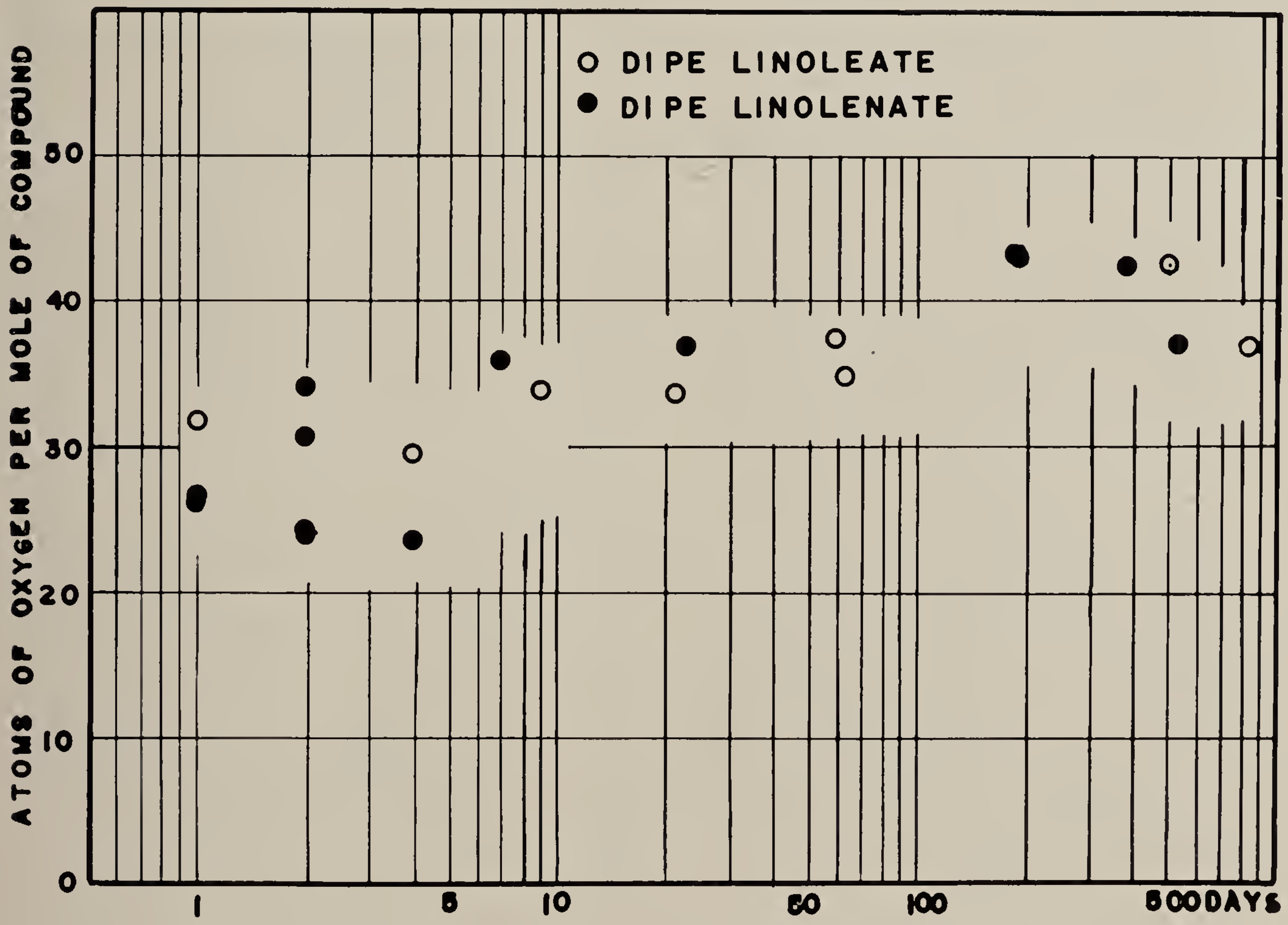


Fig. IV-24. Oxygen content of drying films of DiPE esters.

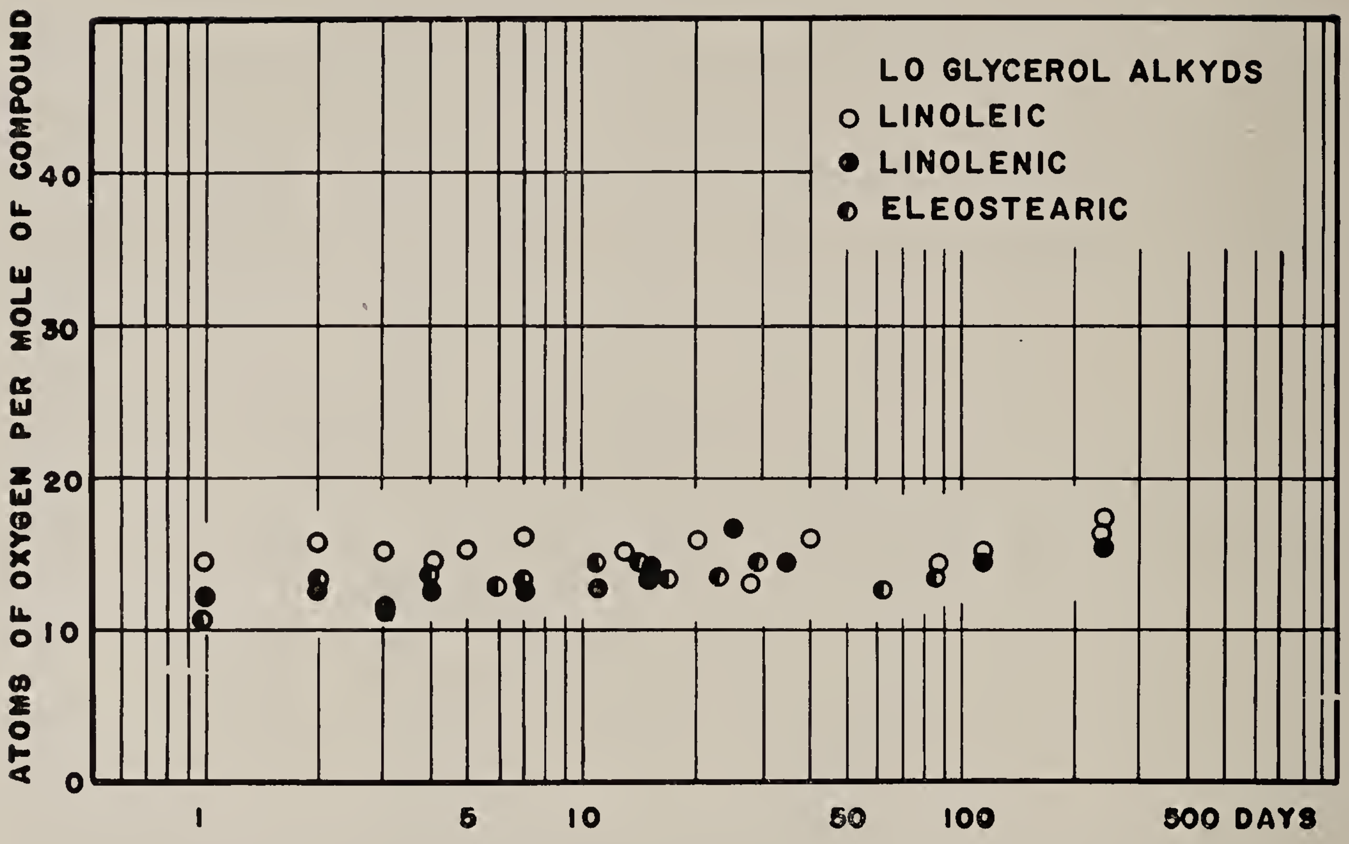


Fig. IV-25. Oxygen content of drying films of LO glycerol alkyds.

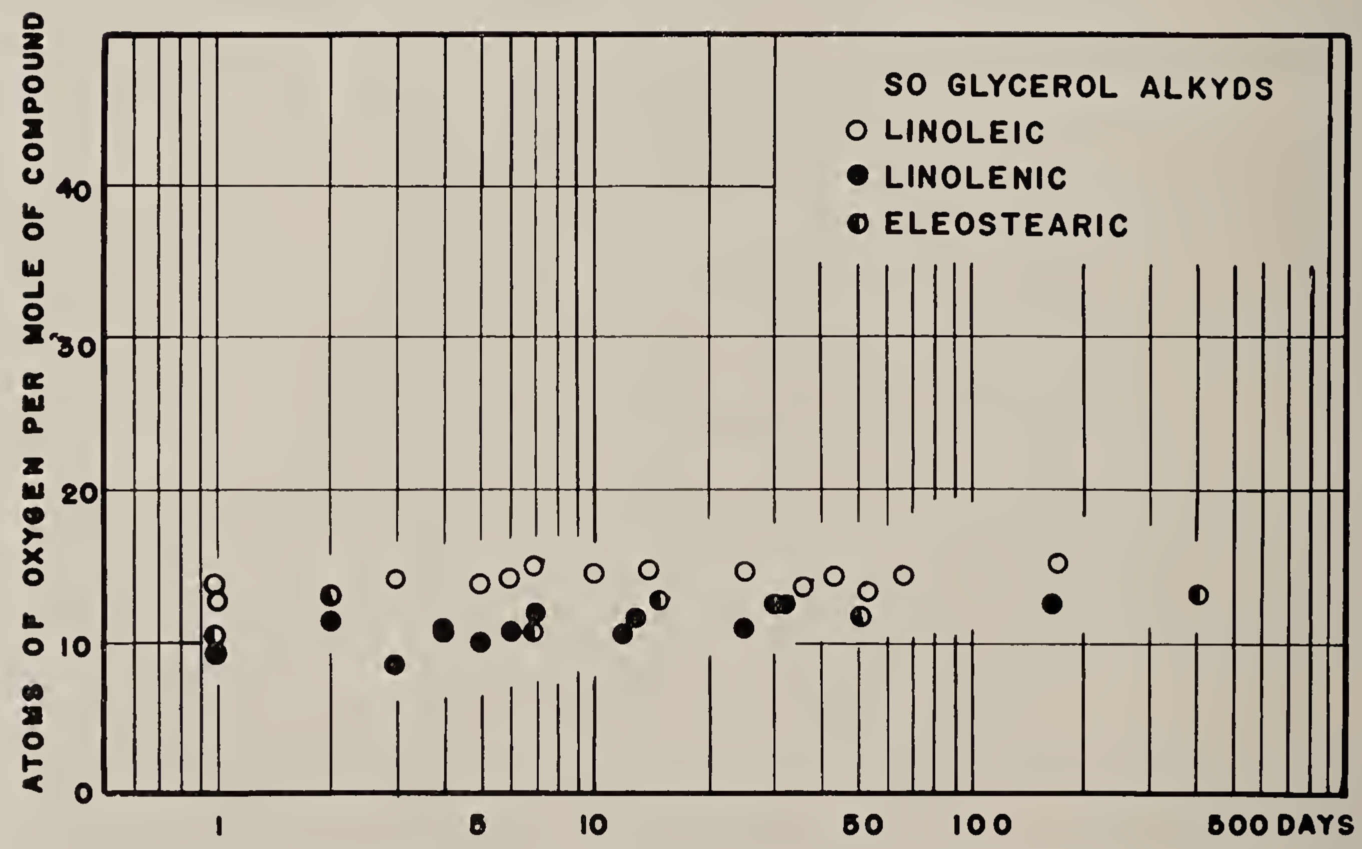


Fig. IV-26. Oxygen content of drying films of SO glycerol alkyds.

in Project 3 was to relate the rate and degree of loss of solubility as directly as possible with the other changes taking place. For this purpose, films dried for varying periods were extracted with a solvent to determine the proportions of soluble and insoluble phases. Natural drying oils contain some constituents which remain permanently liquid and soluble, but it was expected that the synthetic linoleic, linolenic, and eleostearic compounds would in time become almost completely insoluble.

Acetone, ether, and petroleum ether were originally suggested as possible choices for extracting solvent, but experiments to develop the technique, made upon linseed oil films, showed that acetone was too effective as a solvent; it completely dissolved tack-free films (less than 24 hours age) and left residues of only 5% and 7% after 5 and 13 days, respectively. Several other solvents (benzene, methanol, ethyl acetate, petroleum ether, methyl ethyl ketone, and carbon tetrachloride) were tried; all except the last either were too effective or showed a too narrow range of solvent power for good differentiation. Carbon tetrachloride completely dissolved the linseed oil film

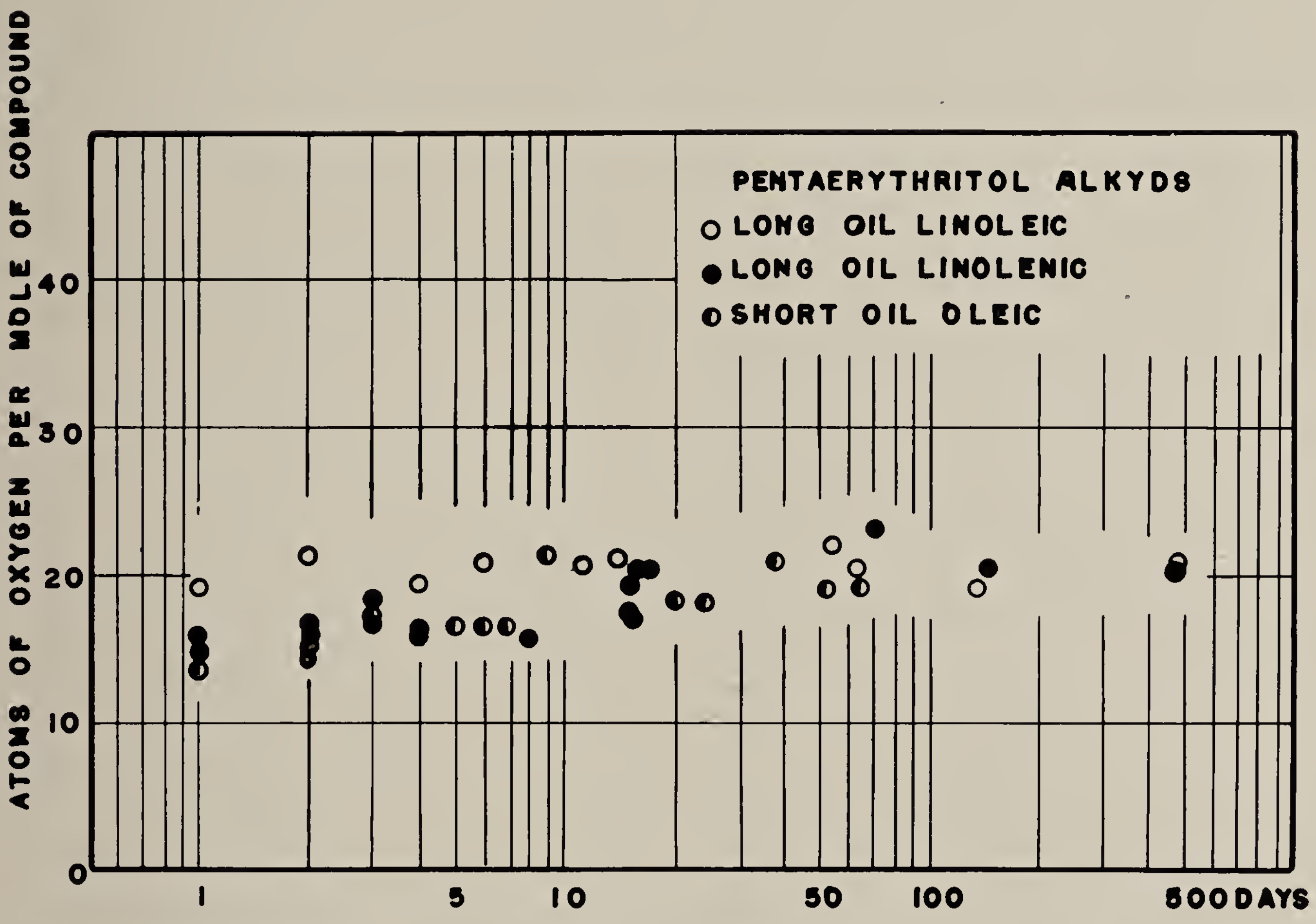


Fig. IV-27. Oxygen content of drying films of PE alkyds.

as it reached the tacky state, but extracted only about 48% after one month. This satisfactory working range, plus its stability, low boiling point, and freedom from fire hazard, all of which were advantageous for the experimental technique involved, led to the choice of this solvent for use with all compounds.

Experimental

About 200 mg. of film, removed carefully and completely by razor blade from the glass plate, was weighed into a fluted cone of Whatman No. 30 filter paper inserted in an extraction thimble. This cone and thimble had been previously extracted with CCl_4 for 18 hours, dried, and weighed in a weighing bottle. The thimble was placed in the siphon cup of a 400-ml. Soxhlet extraction flask and extracted for 18 hours with 80 ml. of carbon tetrachloride, then dried in a vacuum flask held in boiling water for an hour under the reduced pressure of an aspirator, placed in the weighing bottle, and reweighed. The extracted film was used at once for the organic-liquid absorption tests of Project 5.

Discussion

The experimental results, recorded as percentages of the films insoluble on extraction, appear in Table IV-58 and some of them are plotted in Figs. IV-28 to IV-37. In most cases, solubility decreased in a fairly regular pattern, accompanied by embrittlement and more or less discoloration of the residue. Various incidental observations were made. With diPE linolenate, LO linoleic PE alkyd, and LO linolenic PE alkyd, in the early stages of oxidation, the extraction left not the usual coherent film but a strawlike or fibrous structure, as if a linear type of polymerization had occurred. With the last-mentioned compound, this characteristic persisted up to and including the eighth day of cure; it then diminished, as it had earlier with the other compounds, leaving a continuous, evidently well cross-linked, film. Most striking behavior of all was that of the SO oleic PE alkyd. For the first 6 days of cure, its film remained fully soluble; on the seventh day, the insolubility rose abruptly, then gradually increased to a constant value 5 days later. This result was so un-

Table IV-58 and Figs. IV-28 to IV-37 follow.
Text continues on page 107.

TABLE IV-58
Solvent Resistance of Aging Films: Per Cent Insoluble on Extraction with Carbon Tetrachloride

Column *A:* Film age in days.
Column *B:* Percentage insoluble.

Trilinolein

A	*B*
1	41, 44
2	49, 48
4	51, 50
7	59, 56
14	54, 58
28	61, 63
587	85.2

Trilinolenin

A	*B*
1	54.8, 48.8
2	57.3, 56.2
3	62.1, 58.4
4	59.3, 61.3
7	67.8, 67.9
10	75.5, 67.5
14	77.5, 71.0
16	76.0, 78.0
25	73.7, 75.0
66	70.3
108	81.7
130	75.3
144	72.9
210	73.5
582	75.8

Trieleostearin

A	*B*
(3 hr.)	55.5, 54.4
1	53.9, 57.8
2	54.8, 54.1
3	58.5, 59.9
4	56.2, 57.5
7	61.4
10	60.9
14	62.0
21	63.2
29	61.9
227	77.0
232	80.2

PE linoleate

A	*B*
1	49.3, 36.0
2	52.0, 48.8 46.6
4	74.3, 69.6 67.6
7	70.6, 69.5
8	73.3, 74.8
14	77.3
15	77.8, 74.8
113	82.3, 85.8
316	69.6
397	70.5

PE linolenate

A	*B*
2	88.8, 81.0
3	97.3, 98.3
7	77.0, 69.0
14	95.8, 96.6
40	93.8, 90.9
166	90.3
267	80.7
391	79.8
418	80.1
568	96.8

PE eleostearate

A	*B*
(3 hr.)	64.8, 66.4
1	63.3, 62.9
2	62.1, 65.3
3	62.9, 66.0
6	67.1, 67.5
9	68.0
17	68.0
29	74.8
42	71.7
161	78.1
164	79.9
217	77.4
232	79.4
379	81.1

DiPE linoleate

A	*B*
2	80.0, 76.4
4	75.3, 99.6
9	82.3, 65.4
22	72.3, 69.3
56	77.8, 76.1
63	78.4, 69.7
224	78.4
325	75.1
469	77.4
829	79.4

DiPE linolenate

A	*B*
1	77.7, 78.6
2	83.0, 83.8
4	93.8, 91.0
6	82.8, 80.8
7	100.0, 97.4
187	93.6
189	97.2
244	84.1
259	83.2
423	85.7
523	100.0

LO linoleic glycerol alkyd

A	*B*
(4 hr.)	60.8, 58.7
1	65.7, 66.5
2	74.5, 71.7
3	72.3, 68.4
4	73.2
7	75.5
11	79.1
15	77.3, 76.6
22	80.5, 76.8

TABLE IV-58 (*continued*)

Column *A:* Film age in days.
Column *B:* Percentage insoluble.

27	81.8
45	85.0
107	81.7
240	71.8

LO linolenic
glycerol alkyd

A	*B*
(4 hr.)	73.6, 74.0
1	75.5, 76.7
2	76.8
3	75.7, 76.2
4	81.5
5	81.3
7	83.8
10	81.2
14	83.4
15	88.8
19	94.8
24	84.4
38	98.7
48	87.4
86	89.9
242	90.3

LO eleostearic
glycerol alkyd

A	*B*
(3 hr.)	75.3, 75.0
1	76.2, 78.9
2	78.1, 76.4
3	80.4, 78.6
4	86.9, 80.9
7	79.6
11	88.0
14	84.3, 77.8
17	90.9
20	83.9
33	82.4
87	83.4

SO linoleic
glycerol alkyd

A	*B*
$^1/_2$	69.6
1	72.4
2	74.1
4	82.5
5	85.1
6	82.5
7	82.6, 84.5
10	83.0
14	83.5
25	82.0
35	94.6
44	97.5
54	95.1
66	81.6
68	82.6
170	88.9

SO linolenic
glycerol alkyd

A	*B*
(4 hr.)	79.7
1	92.0
2	74.5, 71.5
3	85.7, 80.0
6	78.0
7	78.9
11	79.5
13	86.9
19	87.4
25	85.5
165	87.0

SO eleostearic
glycerol alkyd*

A	*B*
1	69.1
2	67.0
4	66.0
7	66.4
14	78.9
43	84.3
403	91.4

LO oleic PE
alkyd†

A	*B*
235	39.0
321	62.6
336	62.7
482	67.4

LO linoleic PE
alkyd

A	*B*
1	64.8, 64.9
2	68.3, 67.6
5	73.0, 71.6
7	71.5
9	74.9, 75.5
12	72.7, 70.5
15	72.2, 73.3
22	75.3, 77.4
69	73.4
86	76.5
123	79.5
135	76.1
480	77.5

LO linolenic PE
alkyd

A	*B*
1	67.1, 71.1
2	73.5, 72.2
5	91.5, 83.0
8	84.4, 80.3
16	88.8, 85.5
28	80.0, 79.5
41	89.8, 90.3
48	87.4
134	85.7
489	89.3

SO oleic PE alkyd

A	*B*
1–5	0, 0
6	75.6, 22.0
7	82.2
8	86.5, 84.2

TABLE IV-58 (*continued*)

Column *A:* Film age in days.
Column *B:* Percentage insoluble.

A	*B*
9	87.8
13	89.2
15	90.2
20	88.0
24	88.6
35	86.5
38	92.3
52	91.6
64	91.7

Varnish linseed oil

A	*B*
1	40.9, 45.0
2	39.8
3	67.6
4	73.4
5	56.6
6	50.6
7	66.4
9	41.7
11	53.0
15	56.1
21	55.2
28	58.2
35	57.3
53	69.3
65	66.0

Dehydrated castor oil

A	*B*
1	53.9
2	57.5
3	57.3
4	65.3
5	57.2
8	58.0
9	80.1
14	51.1
21	54.7
30	60.3
35	72.5
45	69.1
56	67.2
65	70.2

Commercial alkyd

A	*B*
1	69.0
2	62.1
5	77.9
6	71.1
8	72.1
10	73.1
15	72.6
22	74.1
32	73.4
43	75.0
52	74.6
64	74.9

* This alkyd had gelled in the original vial; partial solution in diisobutyl ketone probably produced a nonuniform film. Results must be considered only approximate.

† Although this film was tacky for a long time, some extractions were made as shown. The figures are of doubtful accuracy but are in the expected range.

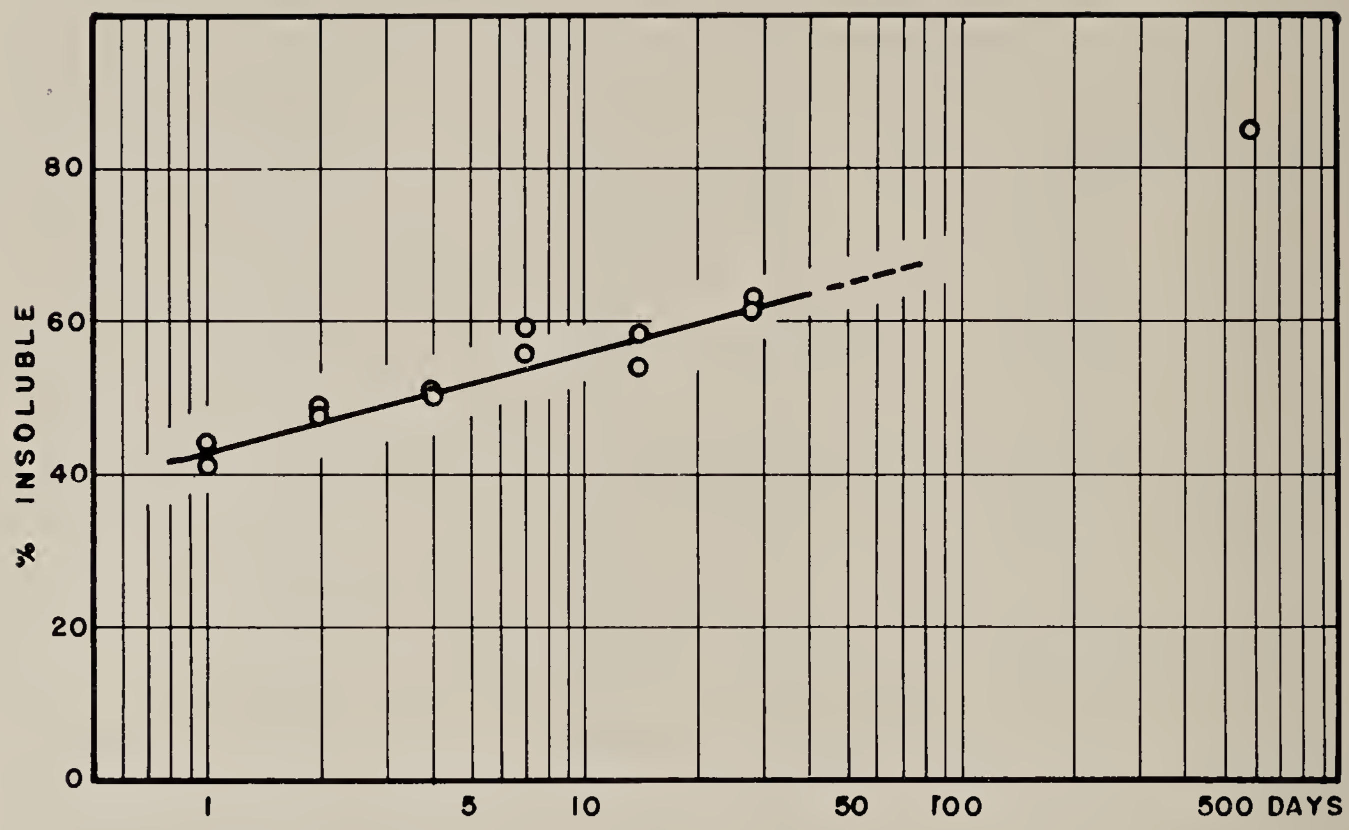


Fig. IV-28. Trilinolein films: loss of solubility in CCl_4 on drying.

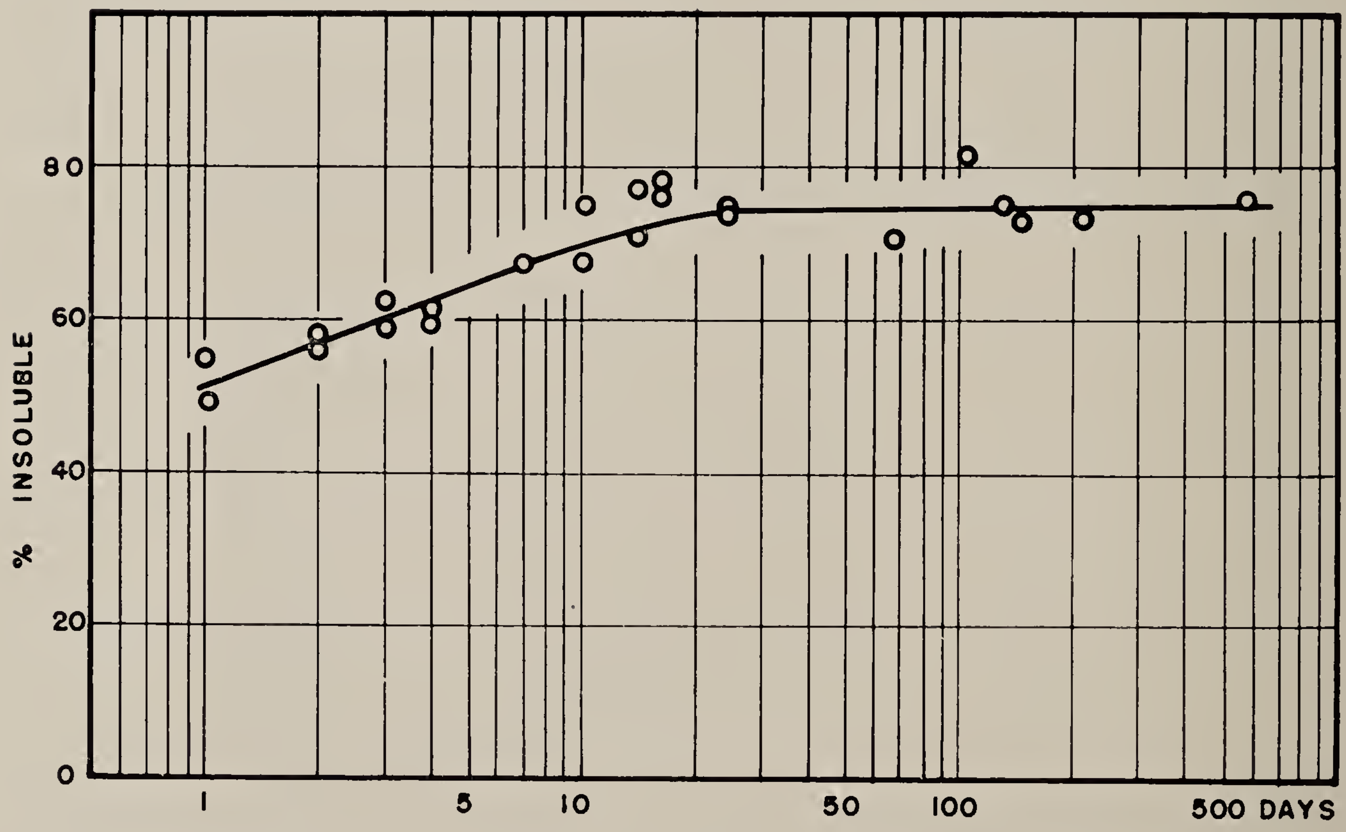


Fig. IV-29. Trilinolenin films: loss of solubility in CCl_4 on drying.

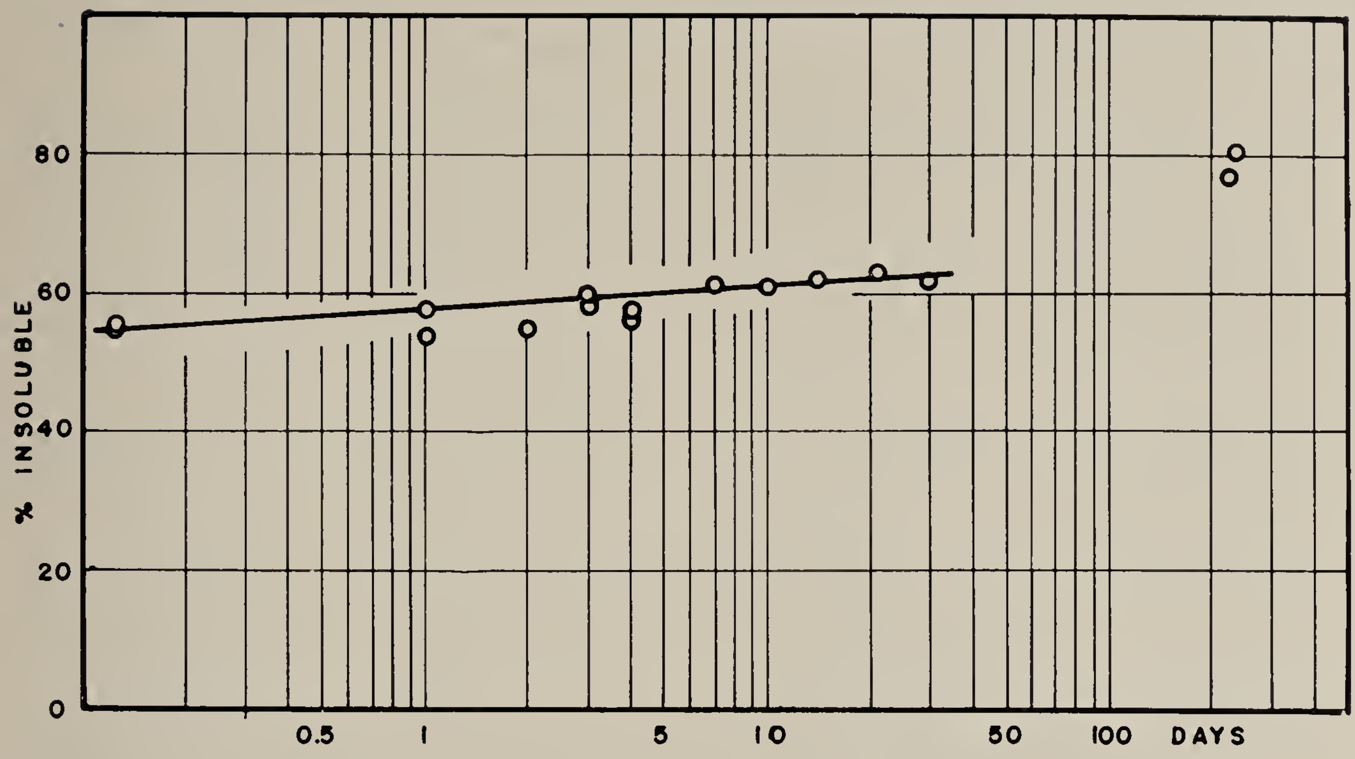


Fig. IV-30. Trieleostearin films: loss of solubility in CCl_4 on drying.

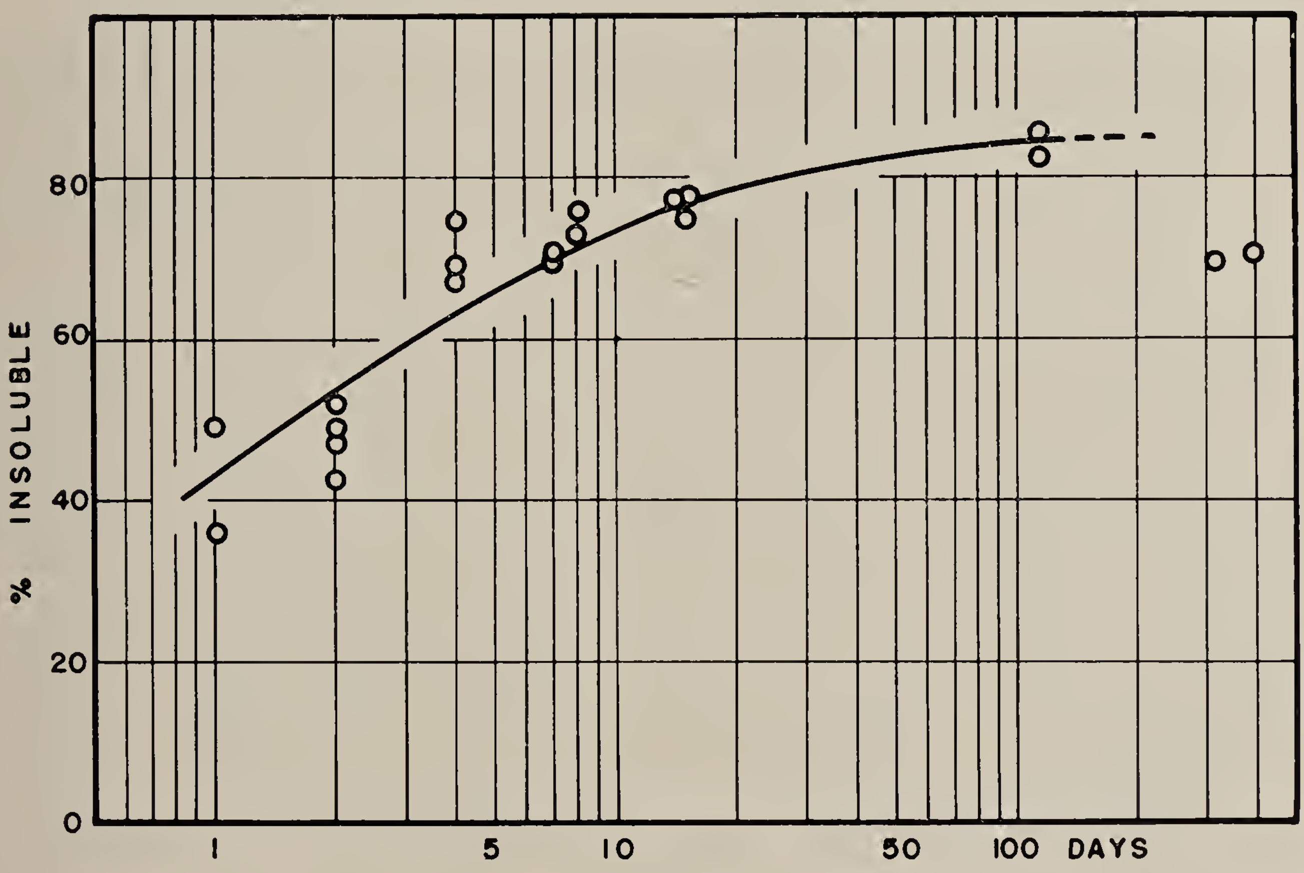


Fig. IV-31. PE linoleate films: loss of solubility in CCl_4 on drying.

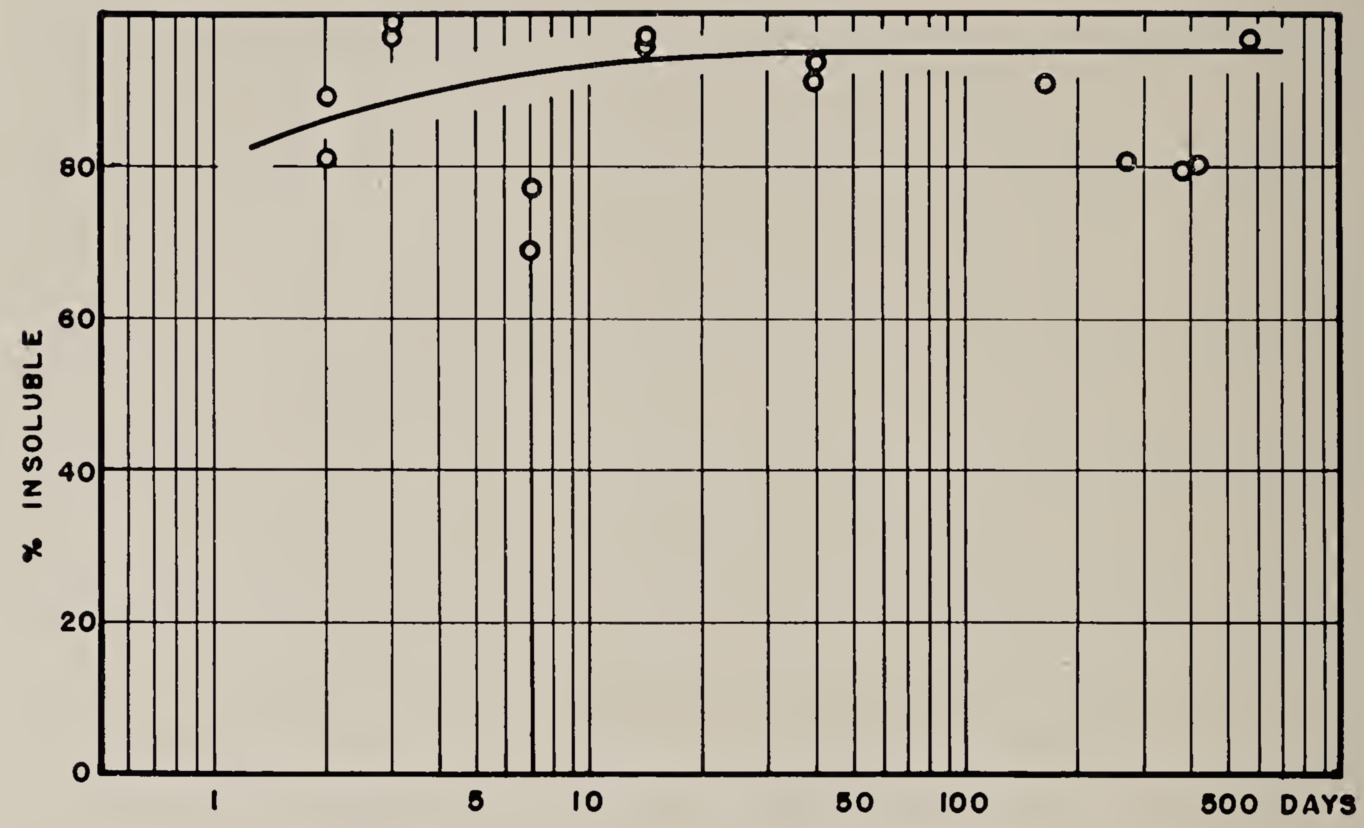


Fig. IV-32. PE linolenate films: loss of solubility in CCl_4 on drying.

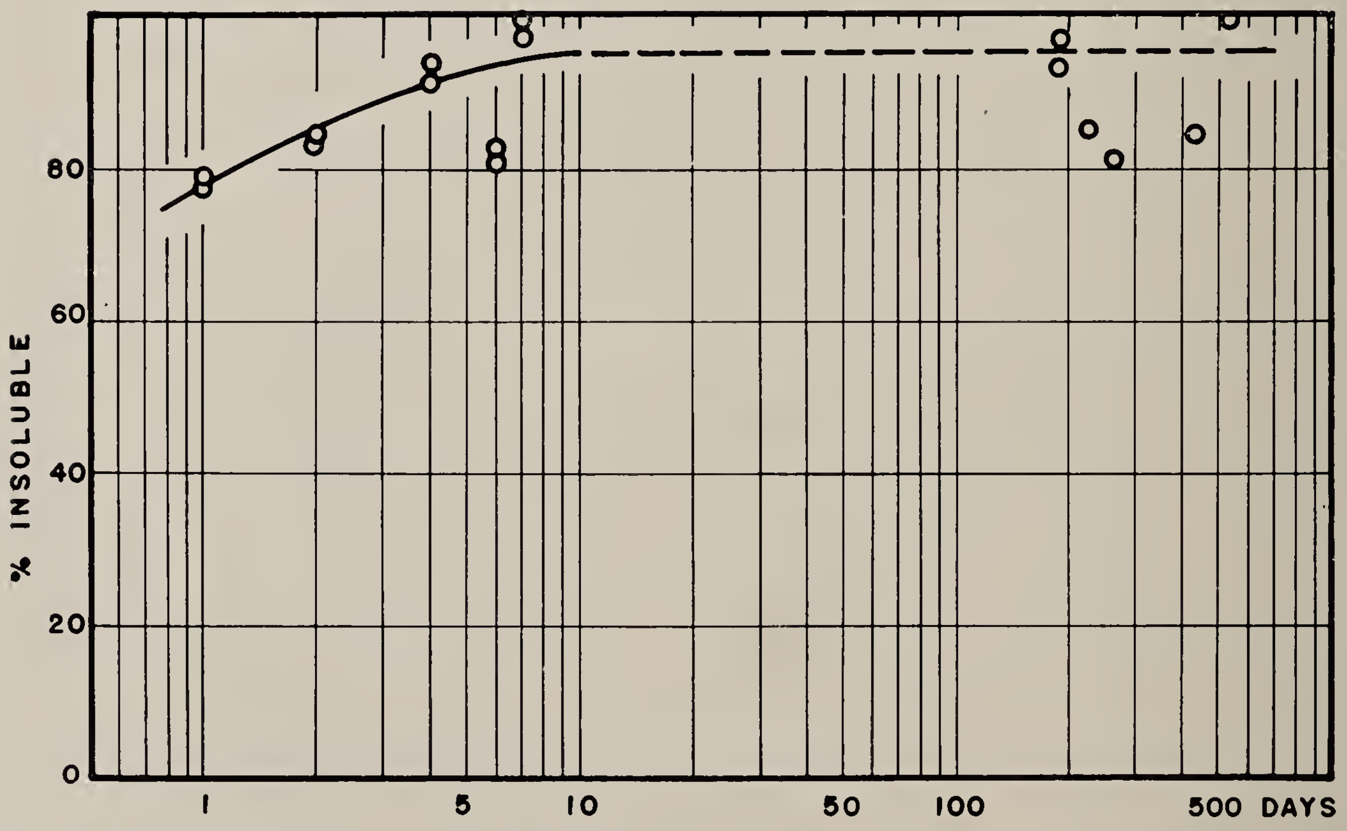


Fig. IV-33. DiPE linolenate films: loss of solubility in CCl_4 on drying.

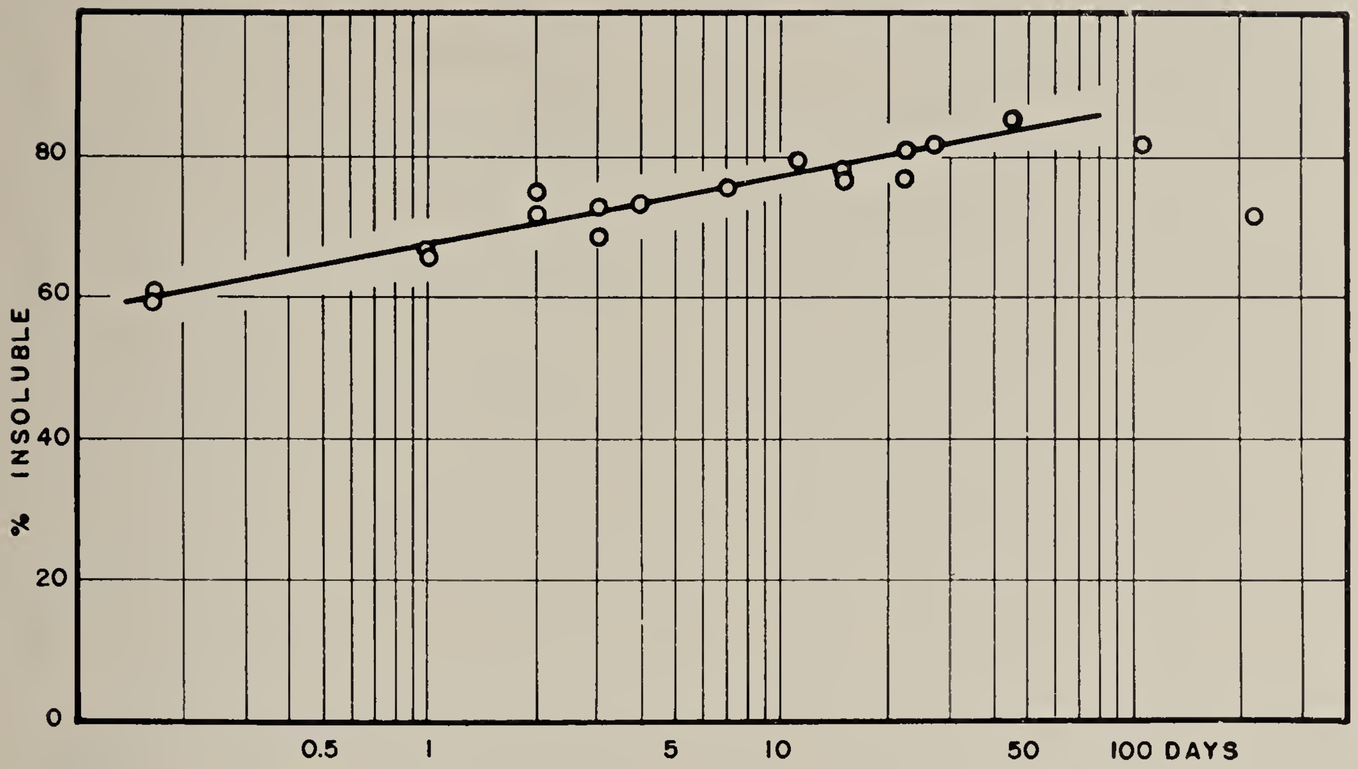


Fig. IV-34. LO linoleic glycerol alkyd films: loss of solubility in CCl_4 on drying.

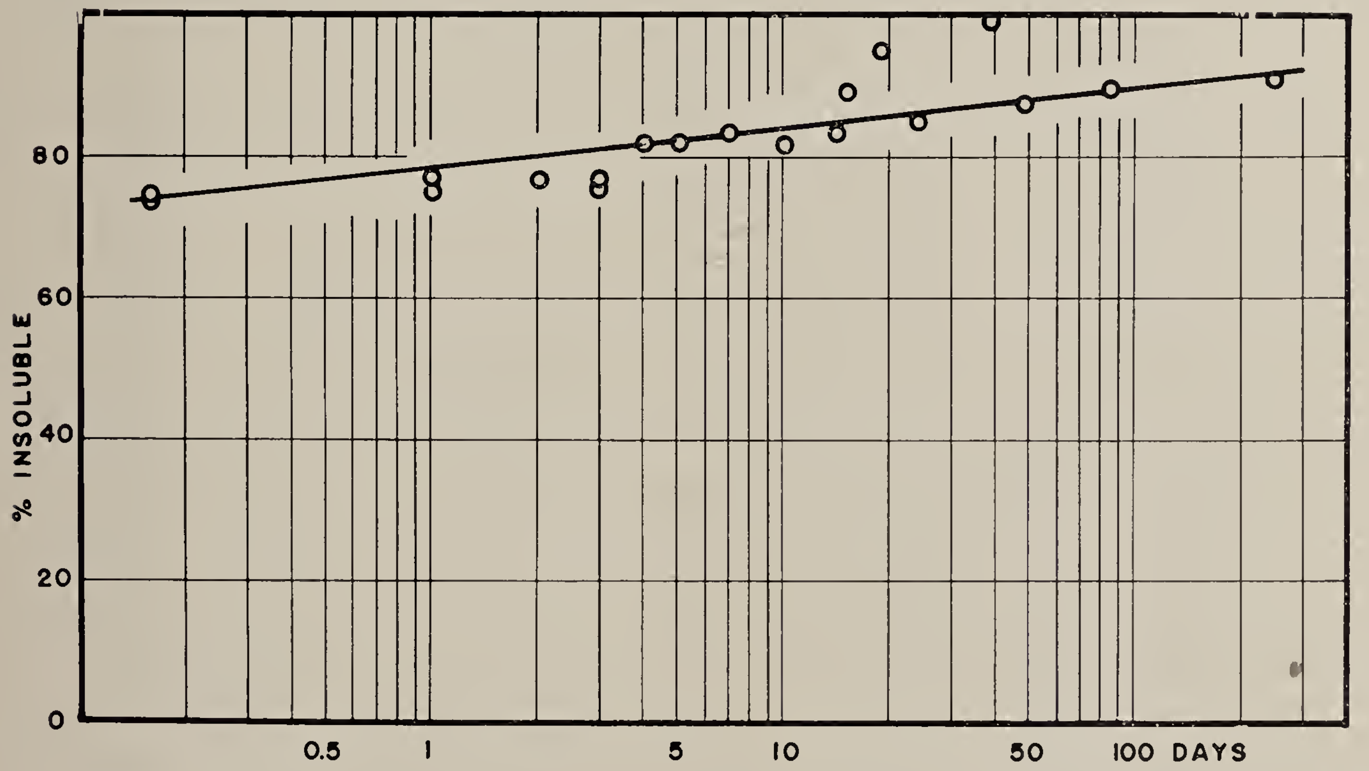


Fig. IV-35. LO linolenic glycerol alkyd films: loss of solubility in CCl_4 on drying.

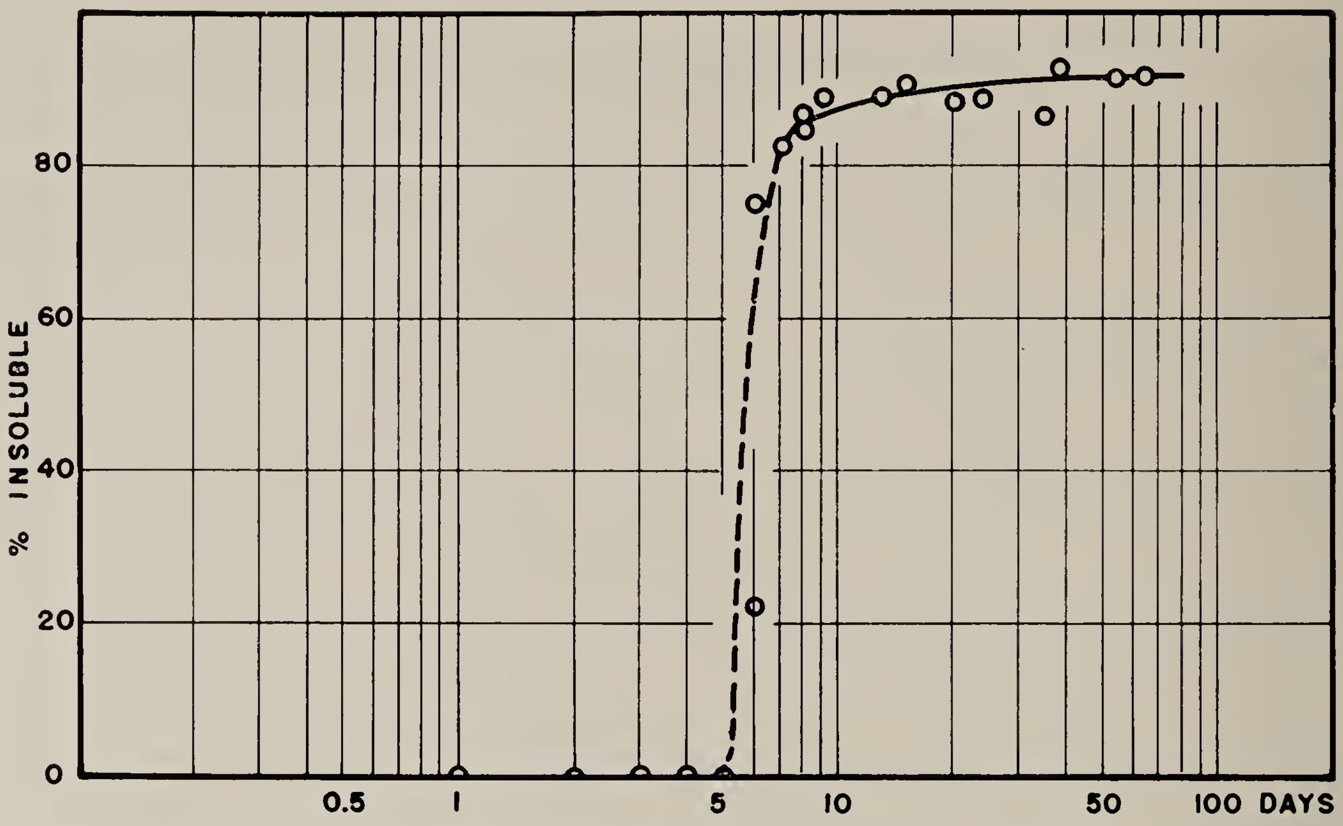


Fig. IV-36. SO oleic PE alkyd films: loss of solubility in CCl_4 on drying.

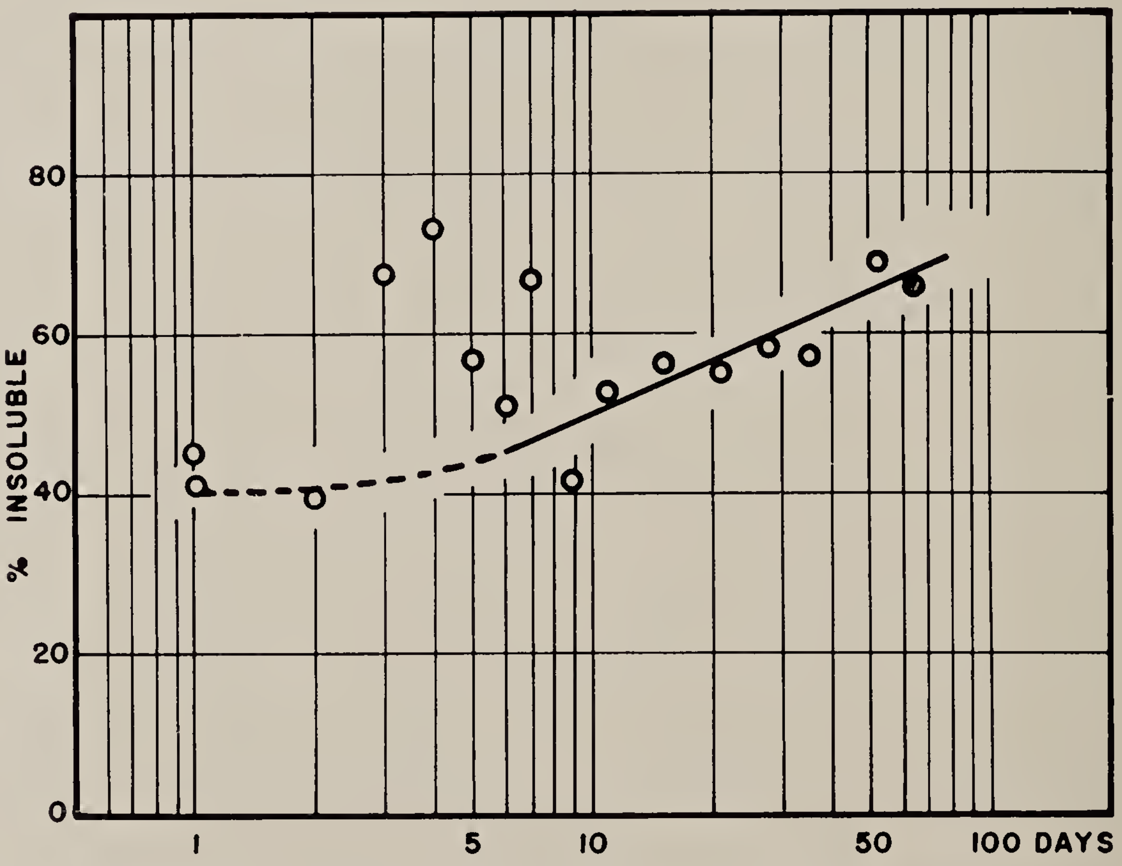


Fig. IV-37. Varnish linseed oil films: loss of solubility in CCl_4 on drying.

expected that a second series of films was laid, and the experiment repeated with similar results. The behavior does, however, correspond with a marked change in the physical character of the film at the sixth day.

The other oleic compounds dried so slowly (if at all) that no reliable results could be obtained. DiPE oleate was 34% insoluble at 71 days, 53.7% at 168, 57.3% at 332; LO oleic PE alkyd, 39% at 235 days, 62.7% at 336, 67.4% at 482. Varnish linseed oil and dehydrated castor oil films at early ages were still semiliquid underneath; they curled and wrinkled in the extraction thimble so that solvent did not make complete contact. After 14 days, the films were more uniform and results more consistent. PE linolenate films, instead of darkening and embrittling, in each case on extraction left a soft, extremely pliable milky white residue.

The linolenate compounds in general gained solvent resistance fastest and reached higher levels, followed by eleostearates, linoleates, and oleates (where run) in that order. The low final levels reached by the linseed oil, dehydrated castor oil, and commercial alkyd are undoubtedly due to the presence of oleic and saturated acid compounds.

Absorptive Properties of Films for Organic Liquids, Project 5—University of Louisville

When a film dries, its strength and cohesive properties are due to the development of a more or less continuous structure (like the steel skeleton of a building), the interstices of which are filled with monomeric and low polymeric material. Extraction of this soluble matter as in Project 3 would leave the skeletal structure which could then absorb more or less of any compatible organic liquid with which it was saturated. By comparing the amounts of liquid imbibed, it was hoped that some light might be thrown on the nature of the structure formed by the different types of pure esters and alkyds; and this was the purpose of Project 5. Oleic acid was selected as the organic liquid to be used.

Experimental

For accuracy, an investigation of this sort requires carefully standardized techniques, which had not been fully worked out during the early stages of the project. The procedure finally adopted was the one which gave the most consistent and reproducible results, as follows:

The dried extracted film from Project 3 was placed in a test tube with excess of oleic acid. The test tube was closed by a rubber stopper, with a glass tube inserted to allow evacuation of air. When bubbling at the surface of the film ceased, the tube was set aside for 24 hours. The film was removed, pressed between filter papers until apparently dry, washed superficially with ligroin, dried, and weighed. Results were reported as absorbed weight per unit weight of film.

Fifteen compounds were tested by this procedure and results are shown in Table IV-59.

Discussion

Even the best of the techniques tried gave results of very limited significance because of its crude and highly empirical nature. Values

TABLE IV-59

Absorption of Oleic Acid by Extracted Films

Column *A:* Film age in days.

Column *B:* Weight absorbed per unit weight of dry film.

Trilinolenin

A	*B*
1	0.284, 0.296
2	0.280, 0.183
3	0.141, 0.238
4	0.229, 0.199
7	0.174, 0.160
16	0.148, 0.152
25	0.176, 0.183
144	0.158
210	0.170

Trieleostearin

A	*B*
(3 hr.)	0.121
1	0.130, 0.104
2	0.096, 0.129
3	0.113, 0.090
4	0.139
7	0.107
10	0.151
14	0.106
21	0.096
29	0.222
51	0.249
72	0.244

PE eleostearate

A	*B*
1	0.106, 0.178
2	0.110
3	0.074, 0.116
6	0.145
17	0.152
29	0.247

LO linoleic glycerol alkyd

A	*B*
(4 hr.)	0.305, 0.299
1	0.332, 0.320
2	0.218, 0.255
3	0.284
4	0.259
7	0.143
27	0.077
45	0.070
107	0.149

LO linolenic glycerol alkyd

A	*B*
(4 hr.)	0.167, 0.172
1	0.166, 0.179
3	0.160, 0.143
4	0.130
5	0.124
7	0.122
10	0.158
86	0.100

TABLE IV-59 (*continued*)

Column *A:* Film age in days.
Column *B:* Weight absorbed per unit weight of dry film.

LO eleostearic glycerol alkyd

A	*B*
(3 hr.)	0.179, 0.178
1	0.290, 0.117
2	0.157
3	0.100, 0.102
4	0.075, 0.173
7	0.104
11	0.078
14	0.073, 0.136
17	0.100
20	0.119
33	0.077

SO linoleic glycerol alkyd

A	*B*
1	0.469
2	0.391
4	0.387
7	0.242
10	0.220
14	0.232
35	0.194
54	0.180
66	0.178

SO linolenic glycerol alkyd

A	*B*
1	0.047
2	0.133
3	0.184
6	0.161
7	0.136
11	0.101
13	0.149
25	0.103

SO eleostearic glycerol alkyd

A	*B*
1	0.234
2	0.205
4	0.248
7	0.195
14	0.196
43	0.113

LO linoleic PE alkyd

A	*B*
1	0.258, 0.238
2	0.230, 0.206
5	0.146, 0.154
7	0.151
9	0.195, 0.143
12	0.179, 0.151
15	0.144, 0.179
22	0.154, 0.160
123	0.142
135	0.135

LO linolenic PE alkyd

A	*B*
1	0.282, 0.245
2	0.222, 0.245
5	0.099, 0.140
8	0.108, 0.147
41	0.103, 0.098

SO oleic PE alkyd

A	*B*
6	0.362
7	0.578
8	0.440
15	0.244
27	0.174
38	0.122
64	0.202

Varnish linseed oil

A	*B*
1	0.304
3	0.160
4	0.130
6	0.145
7	0.200
8	0.163
9	0.166
11	0.144
16	0.164
21	0.242
35	0.279

Dehydrated castor oil

A	*B*
1	0.372
2	0.374
3	0.319
4	0.377
5	0.348
6	0.390
9	0.290
14	0.346
21	0.337
30	0.346
45	0.349
56	0.380
65	0.352

Commercial alkyd

A	*B*
1	0.487
2	0.306
3	0.211
4	0.320
5	0.208
6	0.299
15	0.300
22	0.239
32	0.249
43	0.246
52	0.253
64	0.247

for the materials listed varied from 0.047 to 0.487, and results from duplicate runs differed by as much as 0.180 gram per gram of film. Only general trends appeared. The absorption of liquid decreased with film age; films of linolenic and eleostearic compounds imbibed less than linoleic or oleic, as might be anticipated.

References

1. Natelson, S., S. S. Brodie, and E. B. Conner, *Ind. Eng. Chem., Anal. Ed., 10,* 276, 609 (1938).
2. Scofield, F., *Offic. Dig.,* No. 311, 1012 (1950).
3. Williams, G. C., *Offic. Dig.,* No. 311, 1020 (1950).

CHAPTER V

Spectrophotometric Measurements

Infrared and ultraviolet spectroscopy disclose many aspects of chemical structure and chemical changes that cannot be determined by chemical analysis alone. Infrared absorption in the range of 2 to 15 microns reflects the frequency of vibration between various atoms, arranged in groups, which make up the molecules of the absorbing compound. Absorption bands or peaks have been found to be characteristic of certain structures, such as the C—H stretching bands at 3.4 to 3.5 μ, and the carbonyl (C=O) stretching at around 5.8 μ. On the other hand, various types of structure with resonating electron systems are characterized by absorption in the ultraviolet region. So it was hoped that the appearance, disappearance, or change in intensity of infrared or ultraviolet bands would be of value in studying the chemical changes involved in the drying process. Further, ultraviolet light is known to have a destructive effect upon oil films, and the spectrophotometer, by measuring how much light of each wavelength is harmlessly transmitted and how much is absorbed by films of the pure compounds, should indicate which of them is more subject to decomposition from this cause; their relative tendencies to turn yellow on aging might also correlate with spectral characteristics. It was hoped that a method for the quick evaluation of the probable durability of new vehicles might be thus developed. Dr. Long had had some preliminary readings made at the Hercules Experiment Station of a number of films of commercial materials, which gave promise along this line.

Four groups contributed data on infrared spectroscopy, two on ultraviolet. They studied, for the most part, different compounds, and used different instruments and different techniques. All met certain difficulties which required time-consuming development of special equipment and special methods of test. This limited the amount of actual spectrophotometric work which could be done on the Federation samples; but the studies overlapped sufficiently to show agreement between the data obtained by the various groups and confirmed the validity of the procedures used. In addition, the development of these tools and procedures (some of which were novel and ingenious) will be of great assistance in future studies.

The groups participating in infrared studies were (*1*) for the Pittsburgh Club (1), R. W. Auxier and K. Adams of the Westinghouse Electric Laboratories and C. E. Wilson of Zimmerman Co.; (*2*) for the New England Club, W. C. Kenyon, J. J. Kirkland, and Selma Rossmassler of Hercules Experiment Station; (*3*) for McGill University (47), Professor R. V. V. Nicholls of the Department of Chemistry, and his graduate student, W. H. Hoffman; (*4*) for The Hormel Institute (20), Dr. J. R. Chipault and Evelyn McMeans. Those taking part in ultraviolet measurements were (*1*) for McGill University, Professor Nicholls with his students H. G. McAdie and David Marshall; (*2*) for The Hormel Institute, Chipault and McMeans. These readings, both IR and UV, at Hormel were a part of Project 24, Oxidation Studies.

The experimental data from these various projects will be presented by groups first, and their general significance discussed later.

Infrared Spectra, Project 6a—Pittsburgh Club

The spectrograph employed was a large double monochromator, built in the Westinghouse laboratories and in use there for several years. It has rock-salt prisms and is so arranged that gratings can be inserted when greater dispersion is desired.

Figure V-1 is a schematic diagram of the optical path. The off-axis mirrors (M_1, M_2), are about 20 cm. in diameter, with a focal length of 1 meter. The two prisms have a base of 15 cm. and height of 10 cm. The double monochromator minimizes the difficulties sometimes arising from stray radiation, and permits more accurate measurements of per cent transmission in the longer wavelength spectral regions.

If higher resolution is wanted, the gratings (G) may be rotated into the optical path at (G_1); prism No. 1 then serves as a foreprism, or filter, for the grating, eliminating overlapping orders. Selection of slit widths and gain in amplification in the detector enables the spectrograph to provide any type of resolution, comparable with instruments having lithium or calcium fluoride prisms. By careful adjustment of slits and increased gain in the amplifier it can give very high resolution; however, the many reflecting surfaces and the size of the prisms reduce the total energy of long wavelengths.

The detector is a custom-built high-speed thermocouple with a Model 53 amplifier with a chopper in the beam, both of Perkin-Elmer make. Maintained in a constant-temperature, low-humidity room, the instrument reproduces per cent transmission measurements and constant zero to about ±1%.

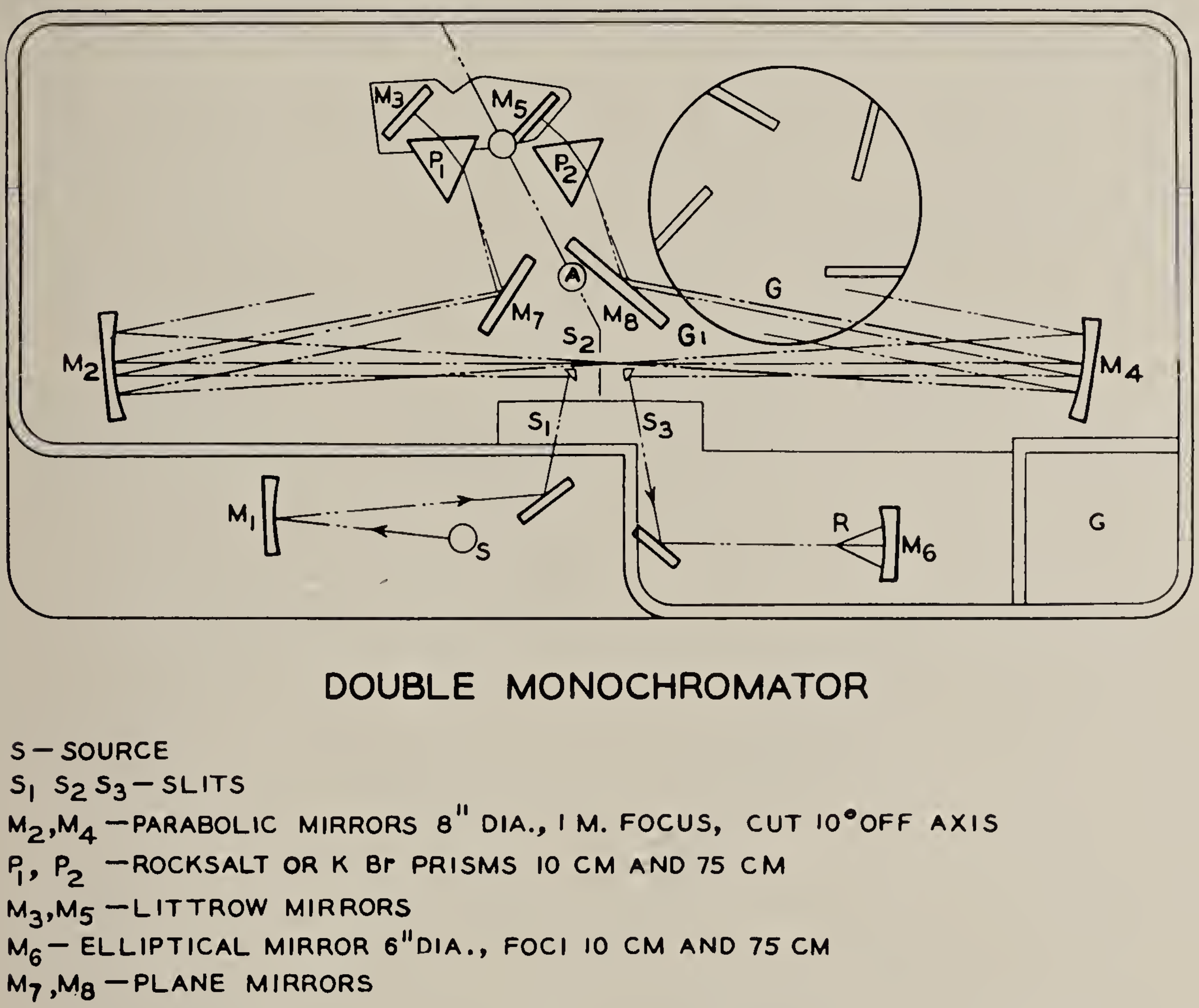

M3
M5
P1
P2
A
G
M7
M8
S2
G1
M2
M4
S1
S3
M1
S
R
M6
G
DOUBLE MONOCHROMATOR
S — SOURCE
S1 S2 S3 — SLITS
M2, M4 — PARABOLIC MIRRORS 8" DIA., 1 M. FOCUS, CUT 10° OFF AXIS
P1, P2 — ROCKSALT OR K Br PRISMS 10 CM AND 75 CM
M3, M5 — LITTROW MIRRORS
M6 — ELLIPTICAL MIRROR 6" DIA., FOCI 10 CM AND 75 CM
M7, M8 — PLANE MIRRORS

Fig. V-1. Optical path of Westinghouse infrared spectrograph.

The Federation samples with one or two exceptions were liquid at the beginning of the drying period, and therefore a holder suitable for liquid samples had to be developed; a diagram appears in Fig. V-2. The liquid is placed on the surface of a polished rock-salt slab which is held in horizontal position at all times, and the system of mirrors reflects the beam so that it passes up through the sample and then into the spectrograph. The holder is inserted between the source and the entrance slit.

It had originally been intended to plot data over the entire region from 2μ to 15μ, but preliminary work indicated that major changes occurred in the region from 2 to 4.5μ. Changes in other regions were not so evident, and the amount of work involved in plotting them did not seem justified, especially when certain variations in other wavelength regions due to the condition of the instrument were taken into account.

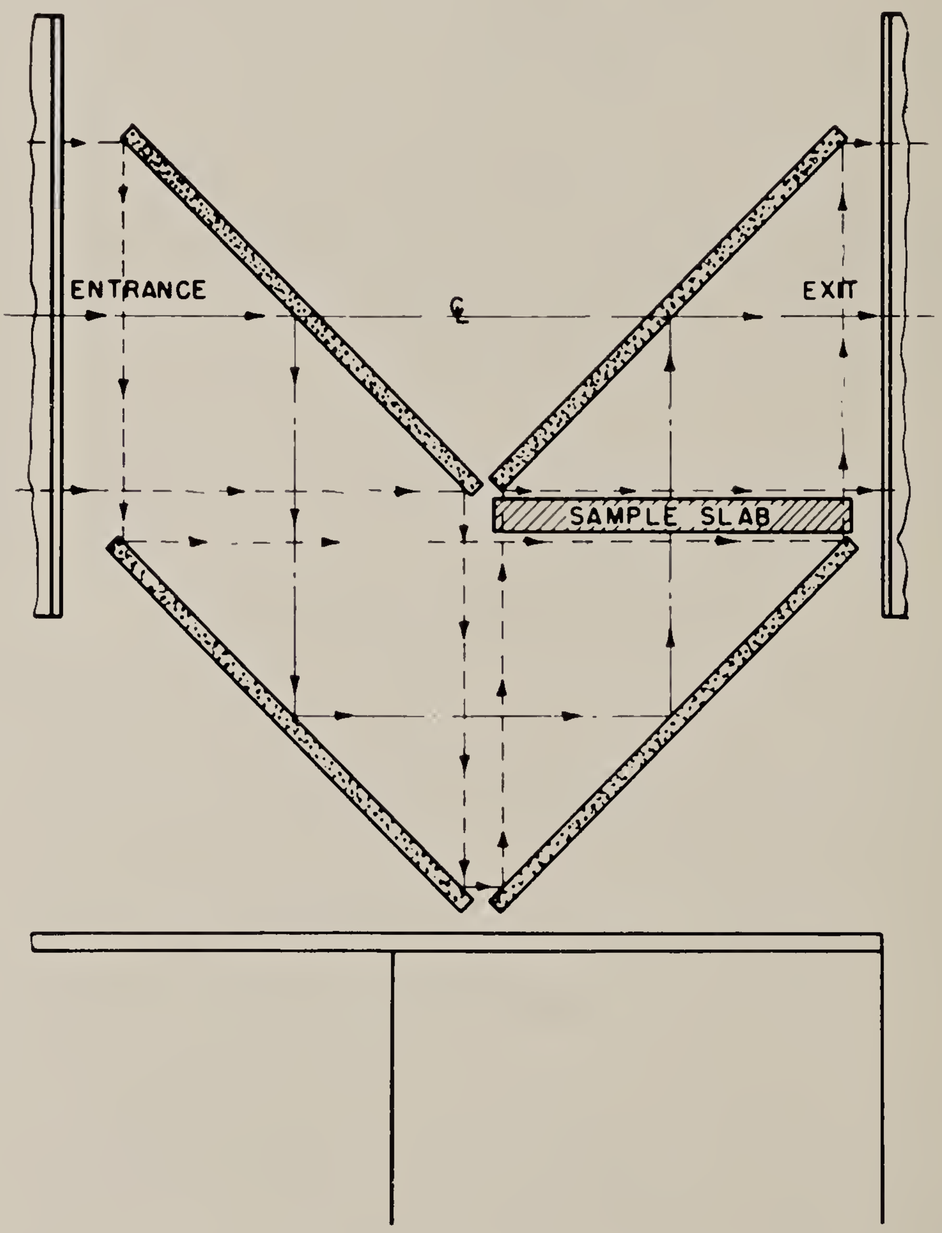


Fig. V-2. Optics of infrared sample holder.

The number of materials studied was also limited. Dr. Lundberg had prepared, as reference compounds for this particular project, dipentaerythrityl stearate (a fully saturated compound) and methyl oleate hydroperoxide, to aid in establishment of the absorption characteristics for the hydroperoxide group in a typical autoxidized fatty ester. The other oils examined were diPE oleate (No. 10), diPE linoleate (No. 11), and diPE linolenate (No. 12); these, with the stearate, providing a series with from 0 to 3 nonconjugated double bonds.

The films were prepared and kept in the constant-temperature low-humidity room, at a fluorescent light intensity of 35 foot-candles. Three or four drops of oil were placed on the surface of the horizontal rock-salt slab within a window of brass shim stock 0.0015 inch thick, and a straight-edge of plate glass was drawn over to remove the excess oil, leaving a film approximately 0.0015 inch thick—the optimum for accurate measurement. Successive readings were made on the same film at the same point, at intervals spaced according to the drying rate of the particular material.

Experimental

Only the initial spectrum (Fig. V-3) of the nondrying stearate was taken. Its two features of interest are the very broad intense band

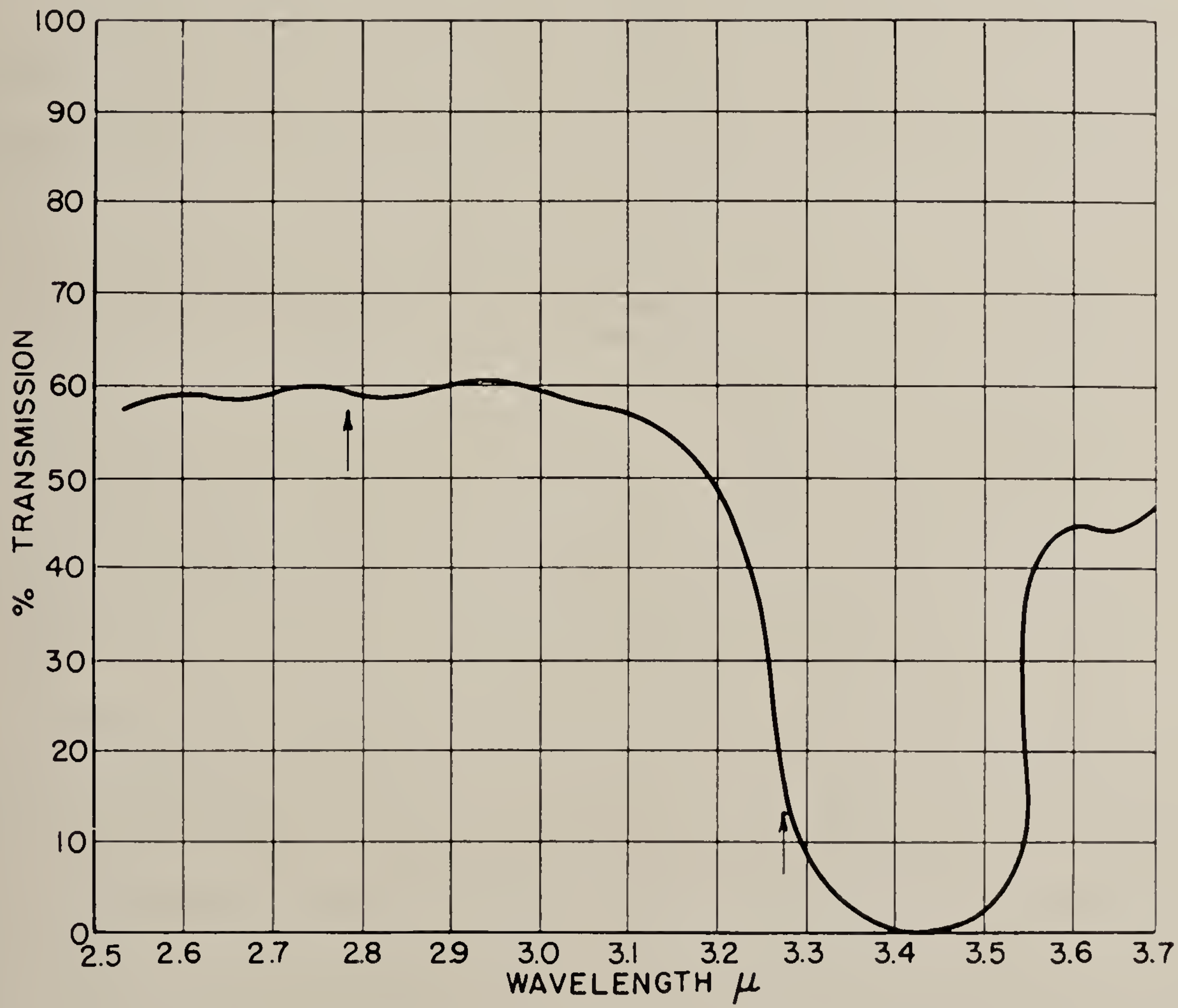


Fig. V-3. Infrared spectrum of diPE stearate.

at about 3.4 μ, attributed to the C—H bond as a stretching frequency, and the almost total lack of absorption in the 2.8-μ region, where one would expect to find absorption due to OH bonds of either alcoholic, carboxyl, or hydroperoxide type. (This spectrum was obtained from a "mull" of the compound in Nujol, since the stearate was insoluble in the solvents used.)

In contrast to this, the methyl oleate hydroperoxide spectrum (Fig. V-4) shows a fairly intense band at about 2.87 μ which is characteristic of peroxide hydroxyl—shifted slightly more toward wavelengths longer than those of other hydroxyl type bands. C—H absorption is also intense but is resolved into the *two* bands generally observed.

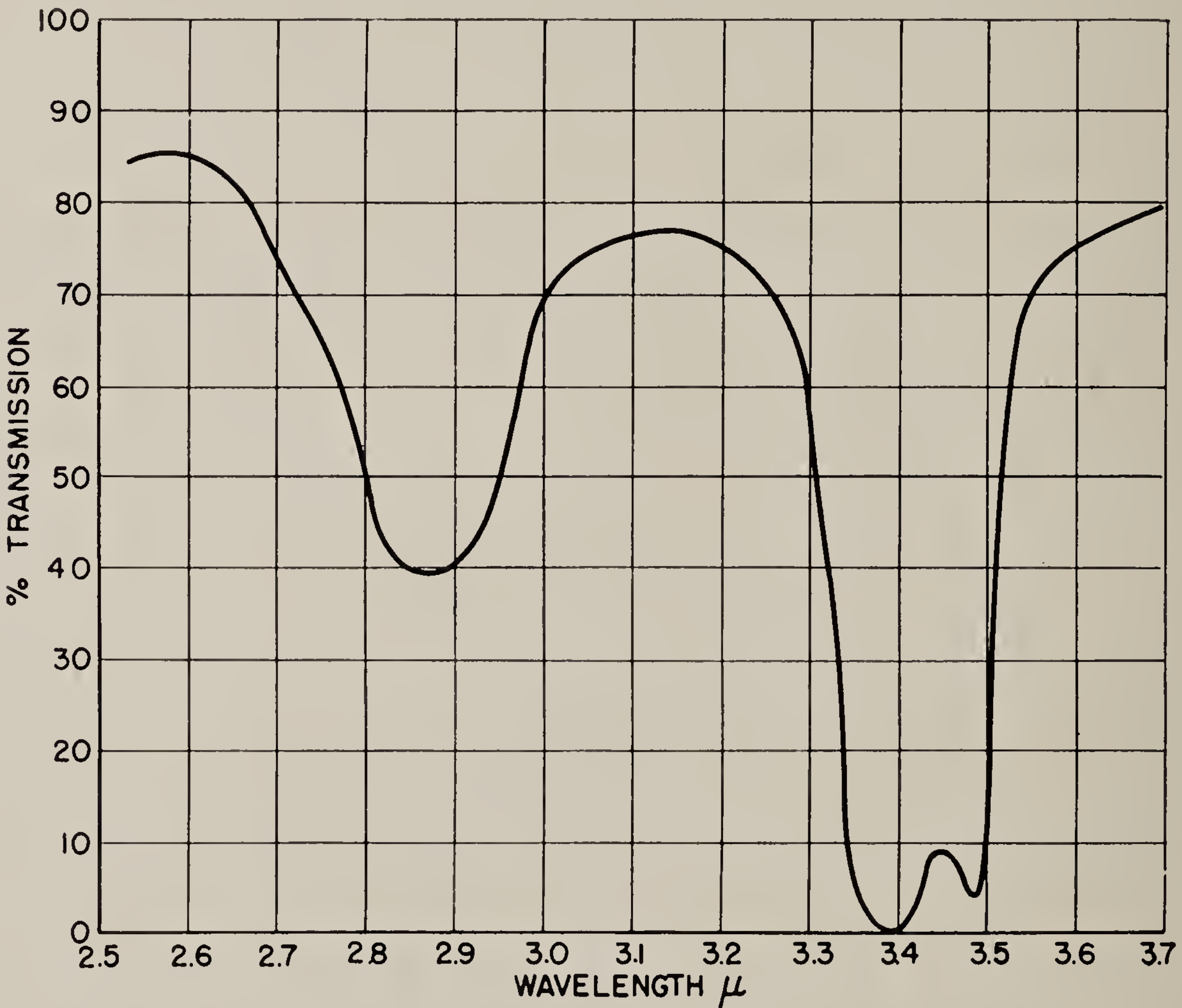


Fig. V-4. Infrared spectrum of methyl oleate hydroperoxide.

Figures V-5, V-6, and V-7 are spectra of diPE oleate at 0, 24, and 264 hours. In the first, to the two expected C—H bands are added indications of absorption at 3.27 and at 2.78 μ. Sutherland (58) assigns the band at 3.27 μ to a C—H absorption peculiar to carbon atoms adjacent to a double bond. The changes in 24 hours (Fig. V-6) are slight and probably not significant. At 264 hours the transmission at both 3.27 μ and at 2.78 to 2.8 μ is a little less; the sample was still liquid and the changes may still not be significant.

Spectra for diPE linoleate appear in Figs. V-8 to V-12. Originally, this compound absorbs only slightly at 2.78 μ but has a definite band at 3.27 μ. The latter band decreases at 24 hours, whereas the former increases; it has nearly disappeared at 72 hours, completely so at 120. Meanwhile, absorption at 2.78 to 2.83 μ increases continuously to the last reading at 168 hours.

DiPE linolenate (Figs. V-13, V-14, V-15) undergoes similar, but even more marked, increases in absorption at the region from 2.78 to 2.83 μ, and disappearance of that at 3.27 μ.

The original intensity of absorption at 3.27 μ differs markedly between the oleate, on the one hand, and linoleate and linolenate, on the other. This supports the view that a methylene carbon between two double bonds is much more susceptible to oxidation than one adjoining a single double bond, with corresponding effect on drying rates.

Infrared Spectra, Project 6b—New England Club

Facilities that this Club had expected to be able to use were found unavailable, but arrangements were finally made with Mr. W. C.

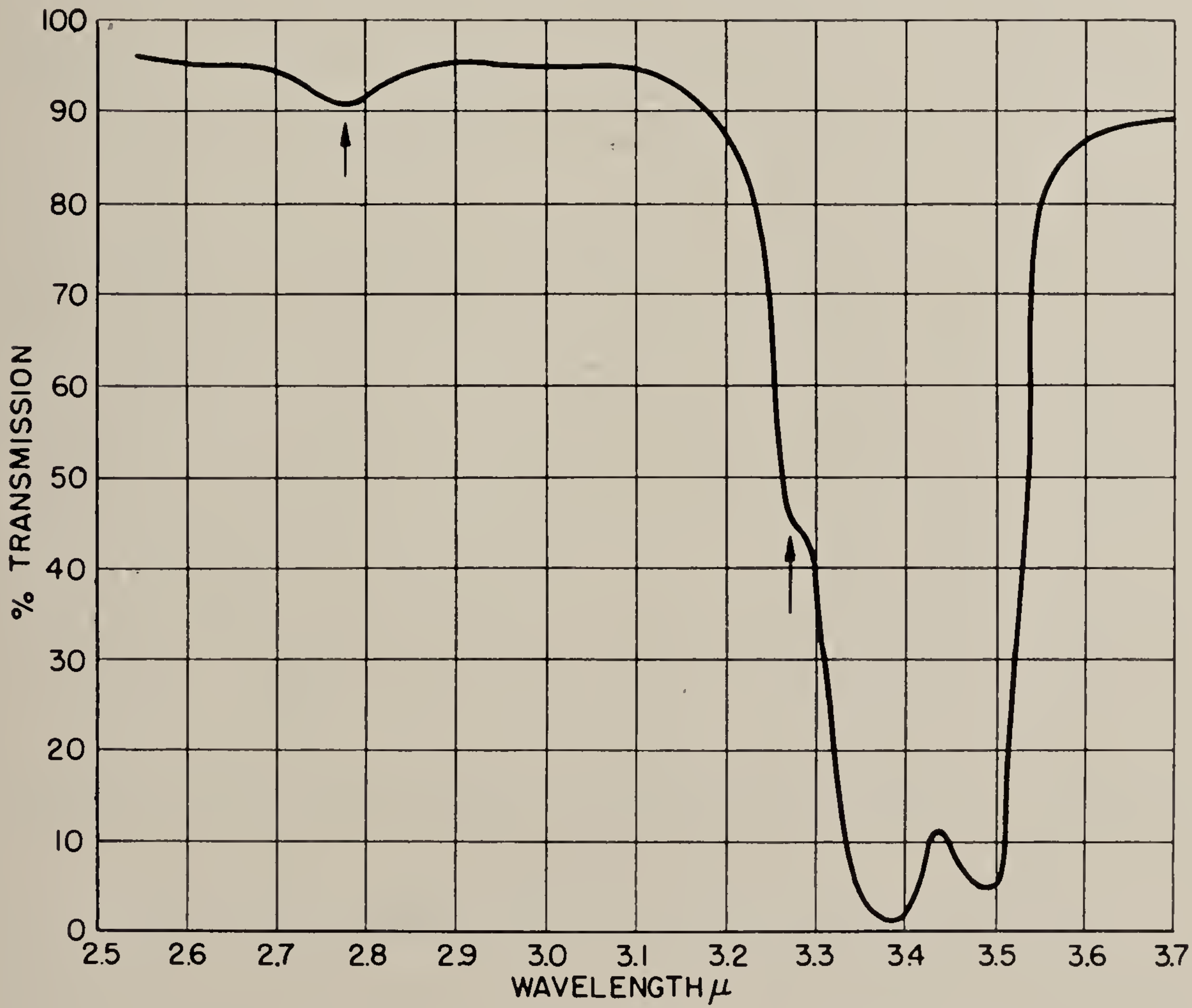


Fig. V-5. Initial infrared spectrum of diPE oleate.

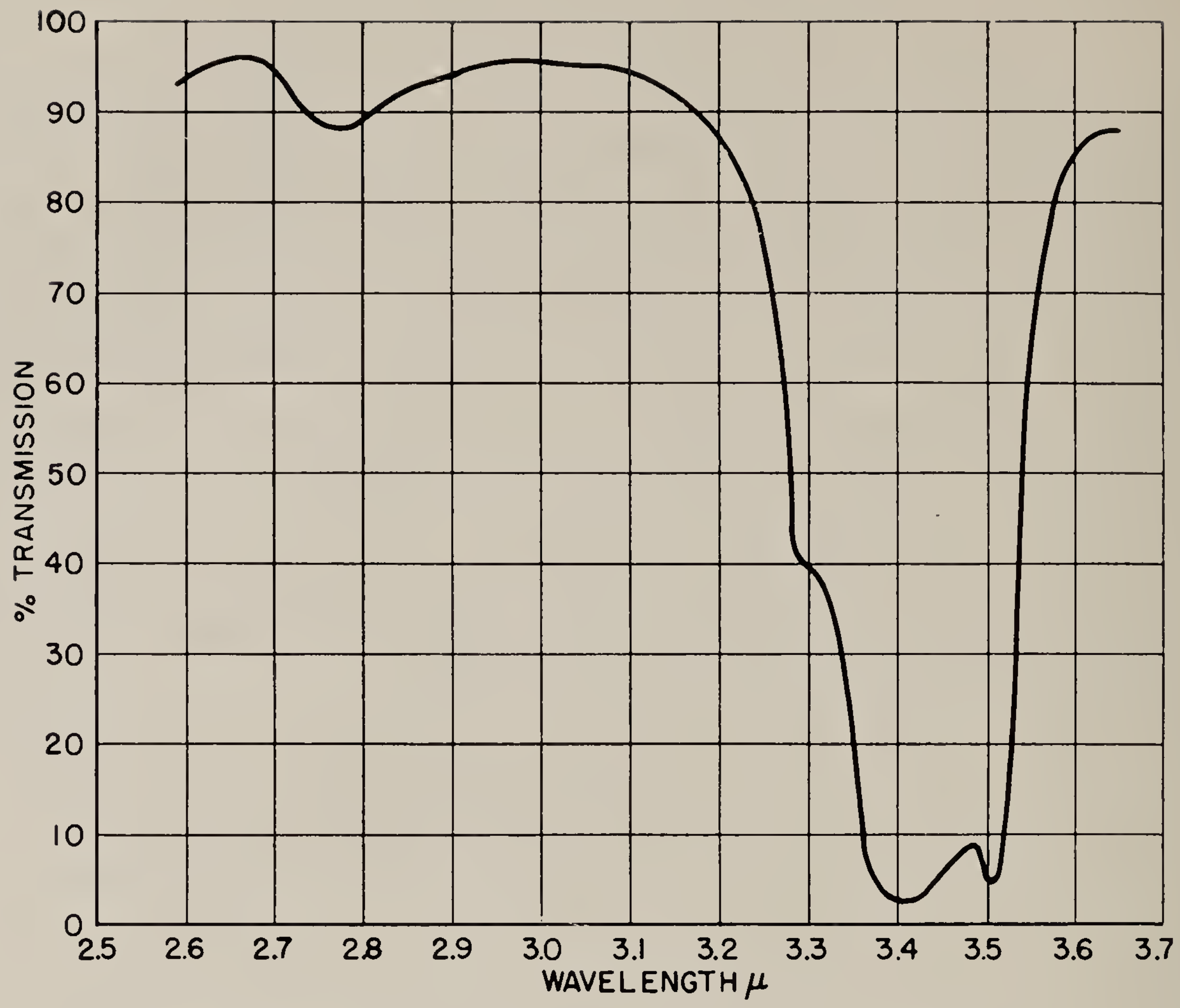


Fig. V-6. Infrared spectrum of diPE oleate at 24 hours.

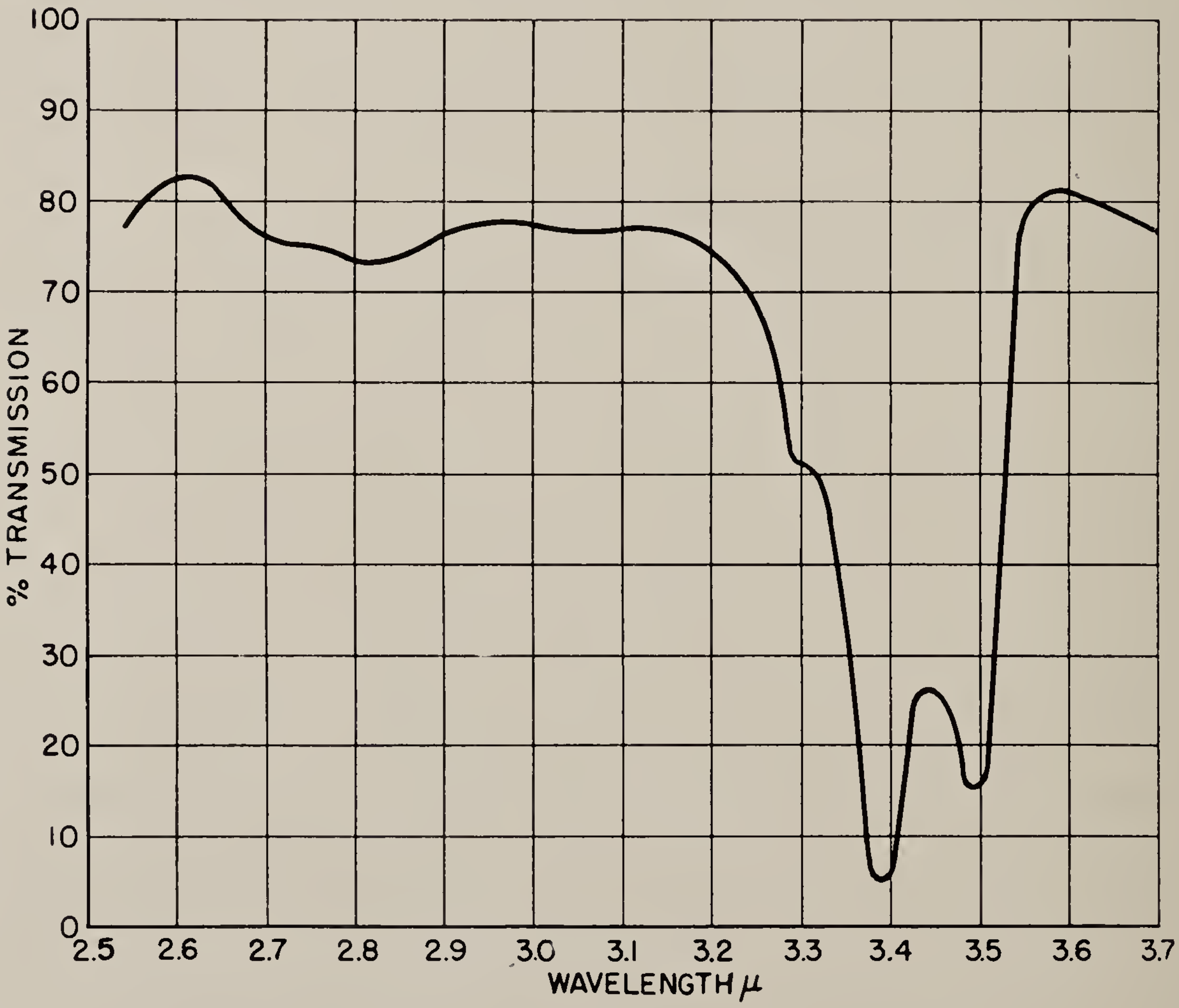


Fig. V-7. Infrared spectrum of diPE oleate at 264 hours.

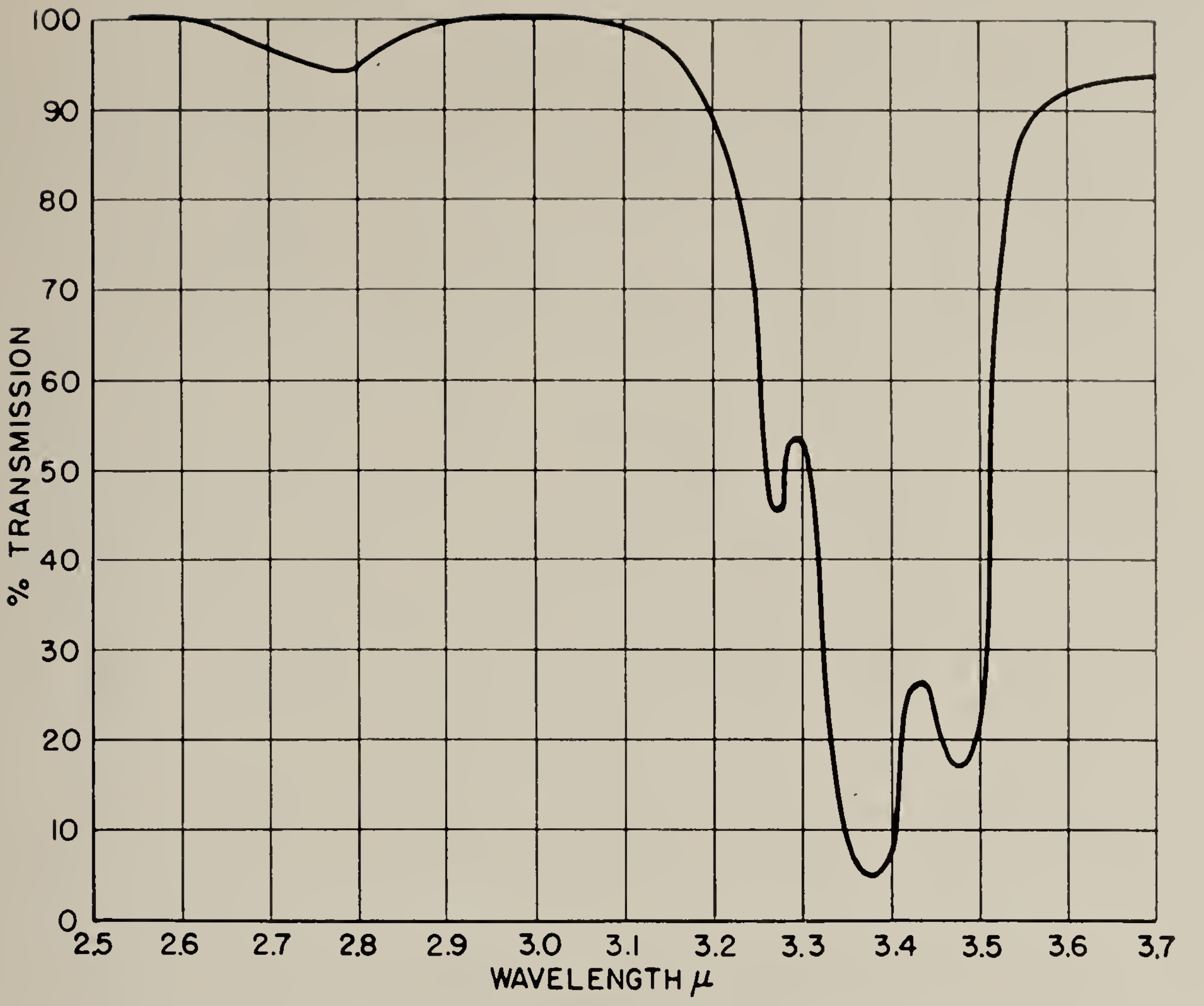


Fig. V-8. Initial infrared spectrum of diPE linoleate.

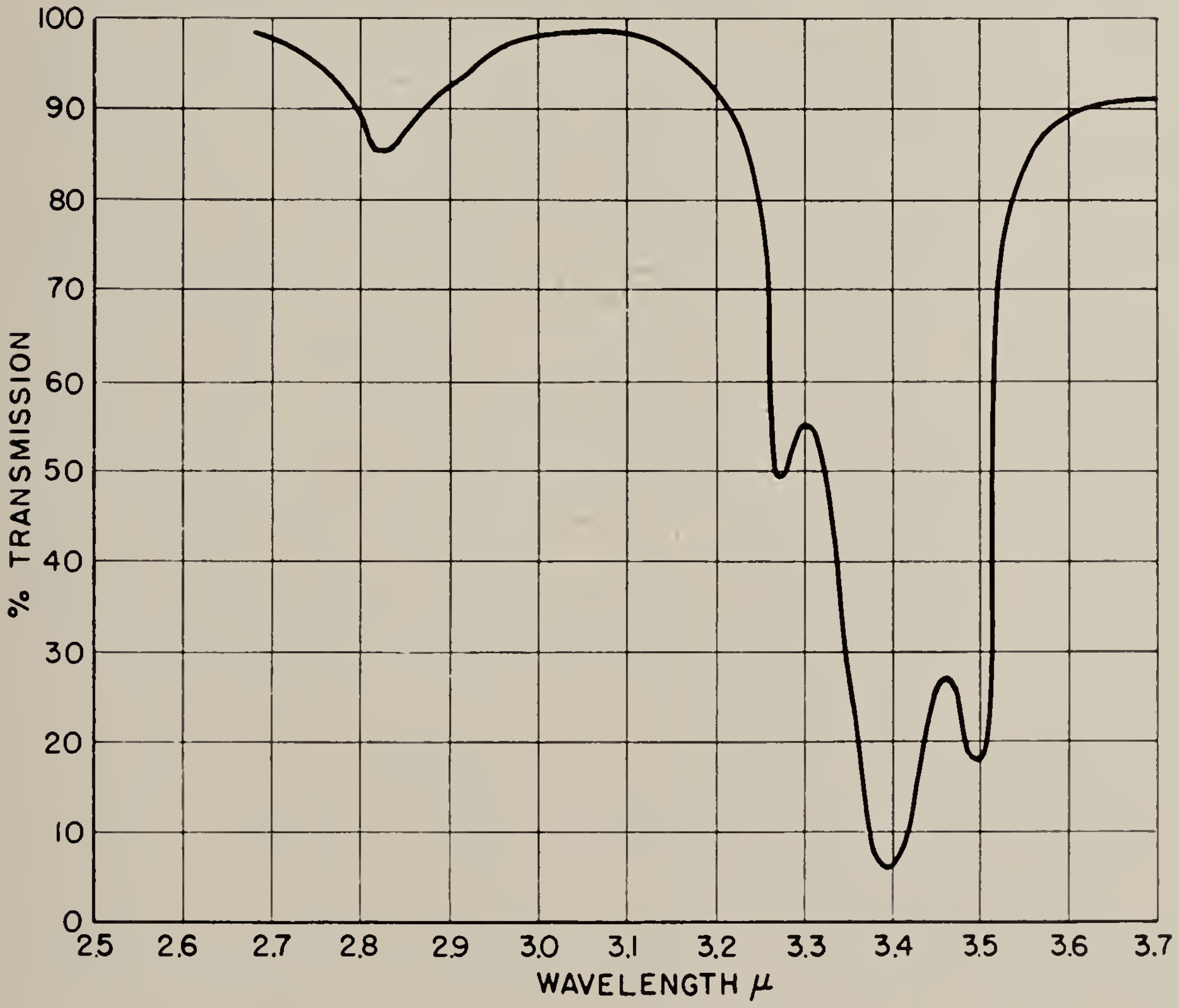


Fig. V-9. Infrared spectrum of diPE linoleate at 24 hours.

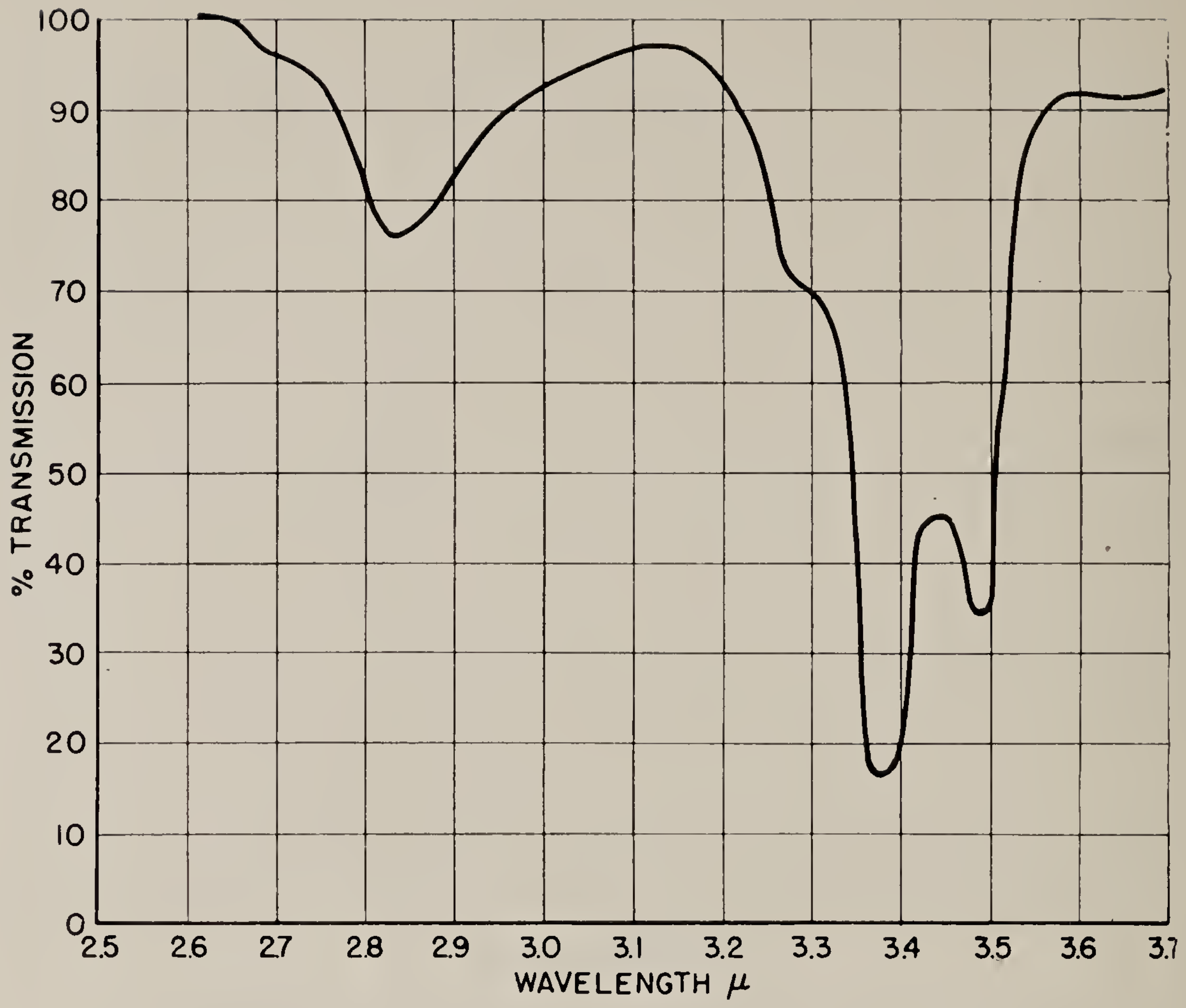


Fig. V-10. Infrared spectrum of diPE linoleate at 72 hours.

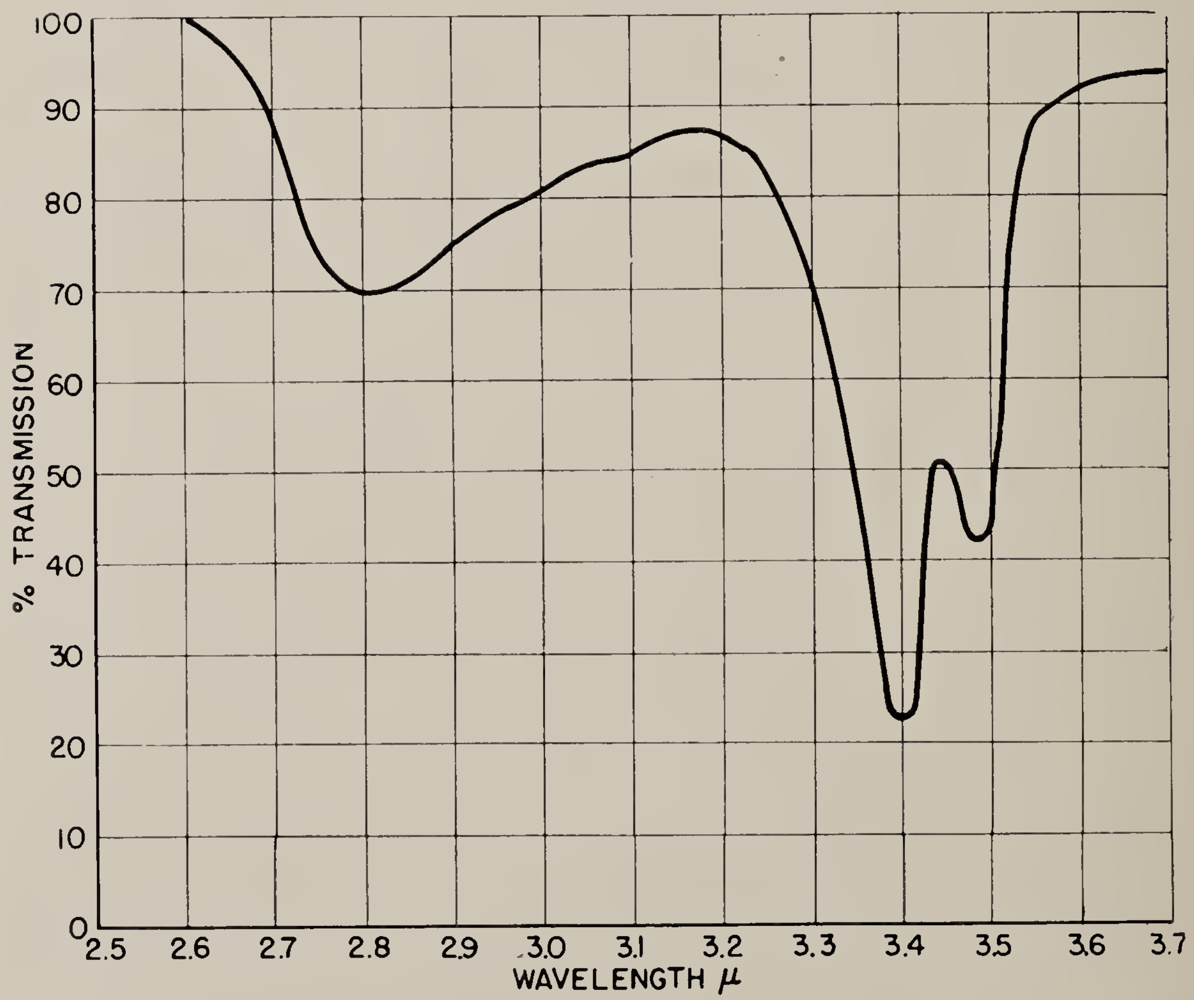


Fig. V-11. Infrared spectrum of diPE linoleate at 120 hours.

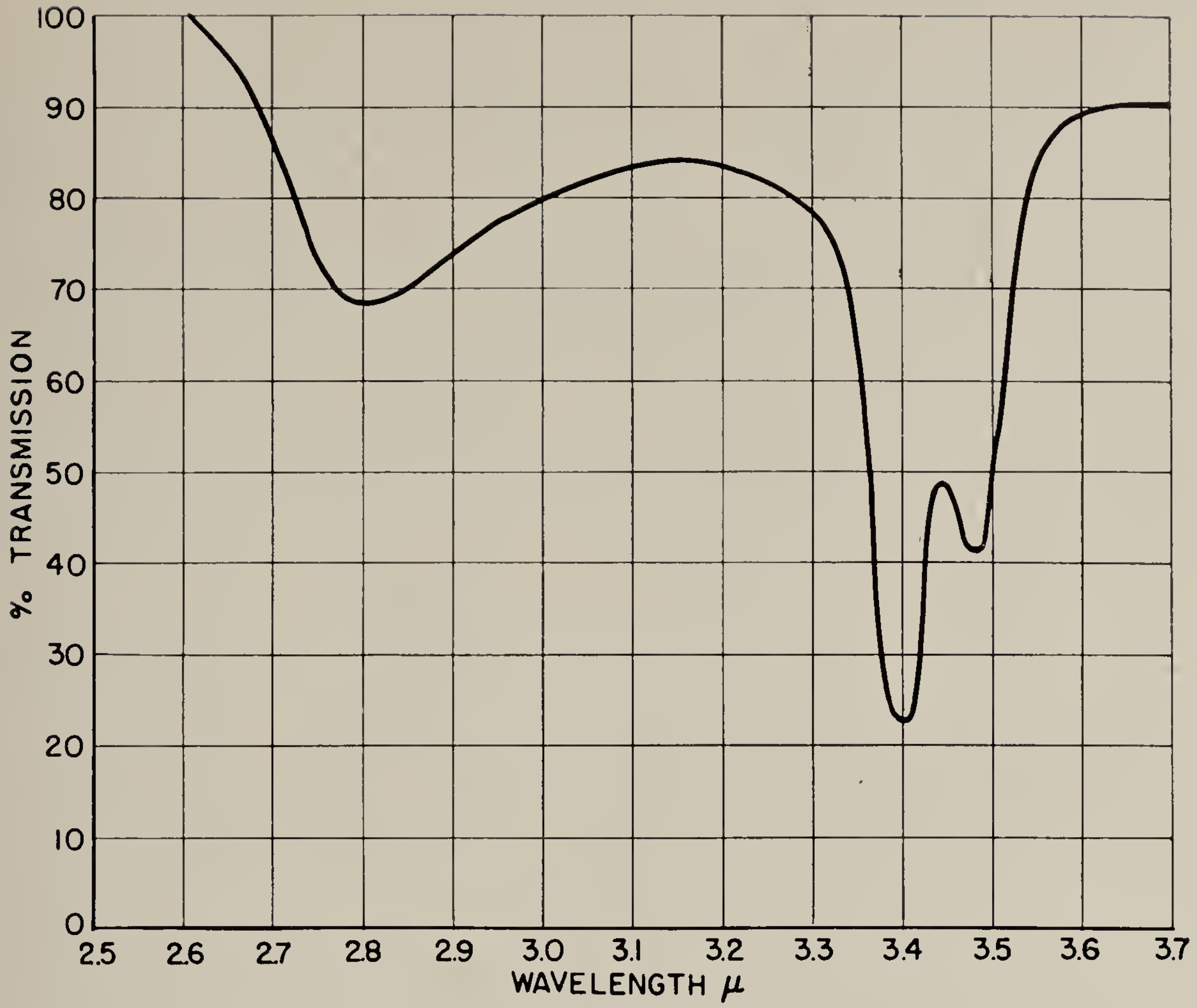


Fig. V-12. Infrared spectrum of diPE linoleate at 168 hours.

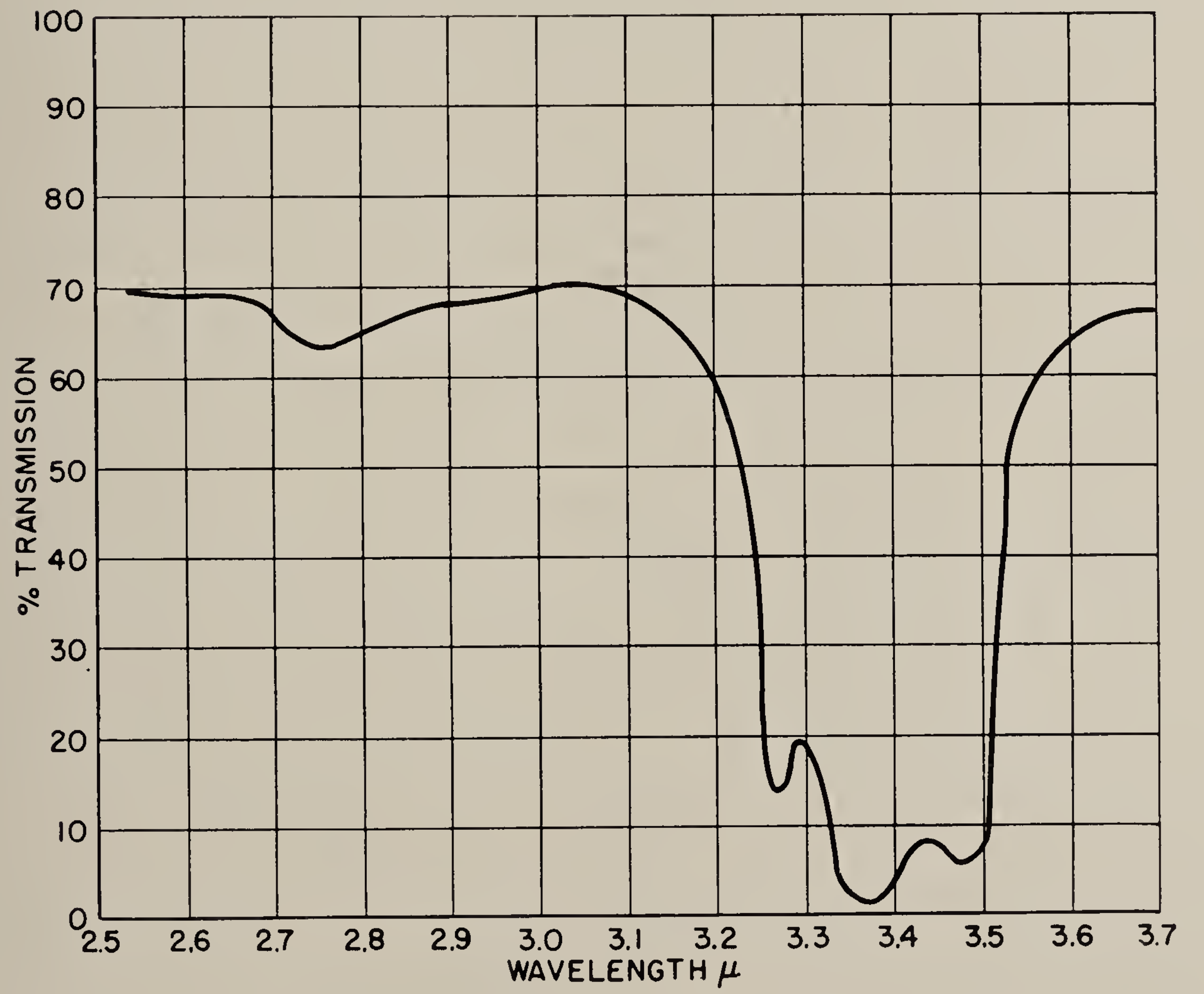


Fig. V-13. Initial infrared spectrum of diPE linolenate.

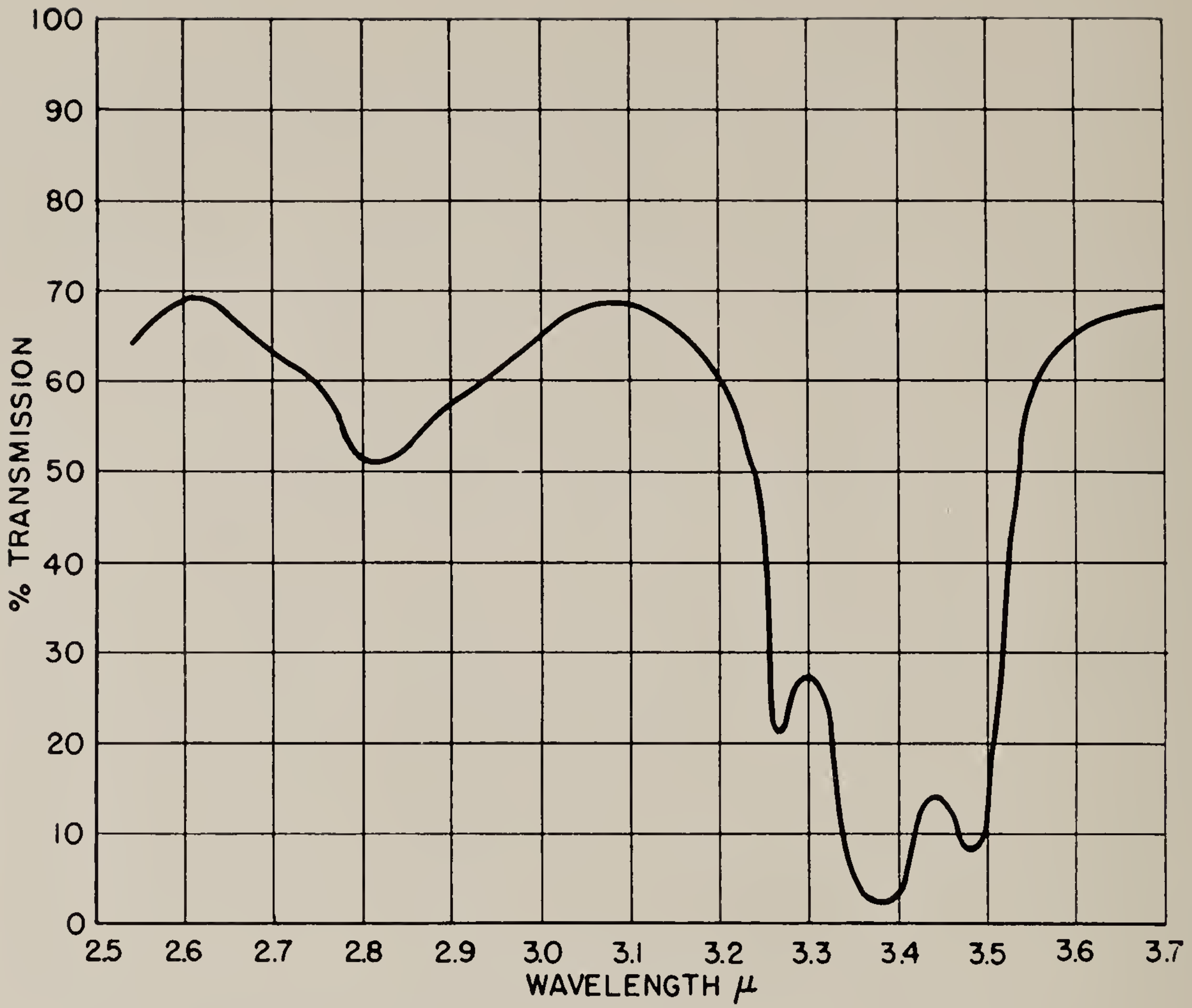


Fig. V-14. Infrared spectrum of diPE linolenate at 20 hours.

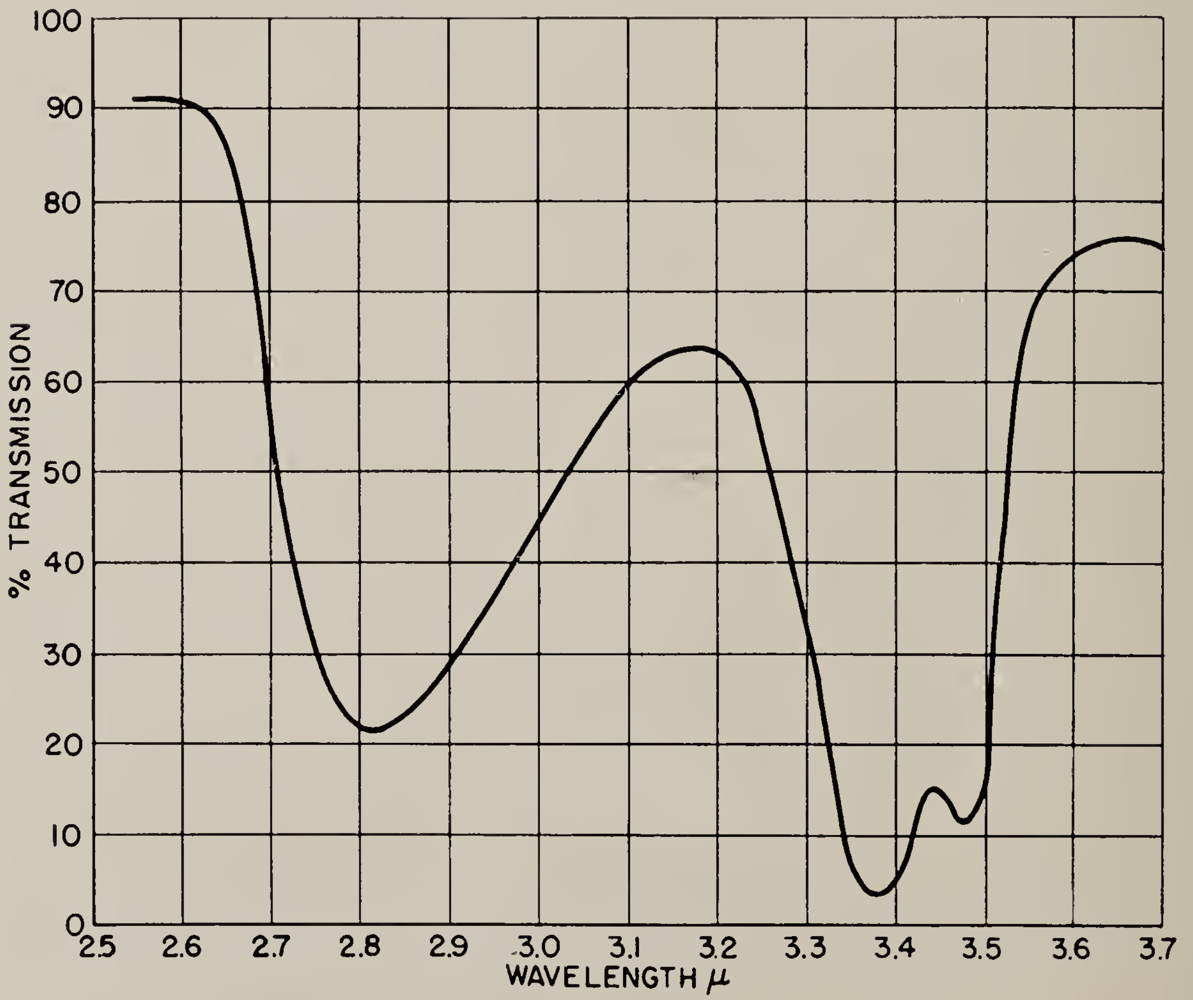


Fig. V-15. Infrared spectrum of diPE linolenate at 96 hours.

Kenyon of Hercules Powder Co. to have readings made at the experiment Station at Wilmington, Delaware, by J. J. Kirkland and Selma Rossmassler. After conferences with Mr. Auxier and Dr. Lundberg it was agreed that the work on Project 6b would be limited to a study of two materials: varnish linseed oil and trilinolein. The Hercules instrument is a Perkin-Elmer Model 21 spectrophotometer, and the settings were: resolution 4, response 1-1, speed 50 sec./μ, gain 6.6, suppression 1, NaCl prism, range 2 to 15 μ, scale 2 in./μ.

Experimental

The films were cast on rock-salt plates in the following manner: a 0.05-mm. copper spacer was placed on a polished rock-salt plate which had been thoroughly washed with toluene or xylene. A drop or two of the sample was then placed on the plate and a straight-edged rock-salt crystal pulled across to doctor the film evenly at the thickness of the copper spacer. The films were aged at the standard temperature, humidity, and illumination conditions.

Because of the tendency of wet films to sag or even run off a vertical plate, the cooperators tried to figure out a way to scan the films in a horizontal position, as the Pittsburgh group had done; but the equipment presented no feasible arrangement for this. Fortunately, it did provide scanning rates rapid enough to let sagging be kept at a minimum, at only a slight sacrifice of precision. Films which sagged during scanning were discarded and replaced with new ones; those which had hardened sufficiently were scanned repeatedly during the aging process. Between runs, the plates were kept on a level block.

The liquid trilinolein sample was kept in two small ground-glass stoppered bottles, sealed with beeswax, under dry nitrogen. It hardened much faster than linseed oil, and its films had less tendency to sag. Both materials showed similar changes on aging: early appearance of hydroperoxide absorption (at about 2.88 μ) followed by that due to materials of other oxidative states (alcohols, aldehydes, acids, etc.), and almost concurrent with this, diminution, at first rapid, then slower, of the band at 3.32 μ, which is probably due to the group =CH—. The change in rate of this diminution occurred at about 72 hours, and the band could no longer be detected after

150 to 200 hours. Further evidence that oxidation at, or adjoining, the double bond group takes place early in the aging process was found in a band at 13.85 μ. A fairly weak band in this region usually indicates a $—CH_2—CH_2—CH_2—CH_2—$ type structure, which, of course, is found in both materials. Fresh films showed a broad, rather strong band here, which later decreased in intensity. It was assumed that part of this band was caused by a *cis*—CH:CH— structure which would be attacked in the oxidative process and, therefore, would result in decreasing absorption as that process progressed. This band attained a rather constant intensity in about the same length of time (150 to 200 hours) as was required for disappearance of the =CH— band at 3.32 μ.

The 5.75 μ band (ascribed to the ester linkage) in both samples broadened toward the longer wavelengths shortly after exposure. This was attributed to additional carbonyl absorption—aldehyde or acid, or both. Bands around 3.8 μ suggesting formation of a carboxylic acid appeared after about 1000 hours, but, as usual, these were much weaker than those produced by the $>C{=}O$ of the carboxyl group at 5.75 μ. Appearance of a broad weak band at about 10.2 μ gave further evidence for formation of carboxylic acid.

In spite of earnest efforts to lay uniform films, the thickness varied too much to permit quantitative comparison of the curves obtained. In order to obtain a fairly accurate measure of aging vs. time, a special technique of analysis was used. It was necessary to assume that absorption due to structures of the $—CH_2—$ type would remain virtually constant. This assumption is justified because of the relative stability of the group against oxidation as compared with groups containing activated hydrogen, and because of the fact that the large number of methylene groups in the molecules would make the ratio of reacted to unreacted methylene groups very small. With the use of this $—CH_2—$ band as a measure of the thickness of the film, it was then possible to compare intensities of the —OH bands in films of different ages. Figure V-16 shows spectra of a varnish linseed oil film at 40 and 692 hours; the critical bands mentioned above are marked. There is some indication from the decreased intensity of the $—CH_2—$ band that the older film is thinner, possibly because, even when level, it tends to draw toward the outer edges of the plate,

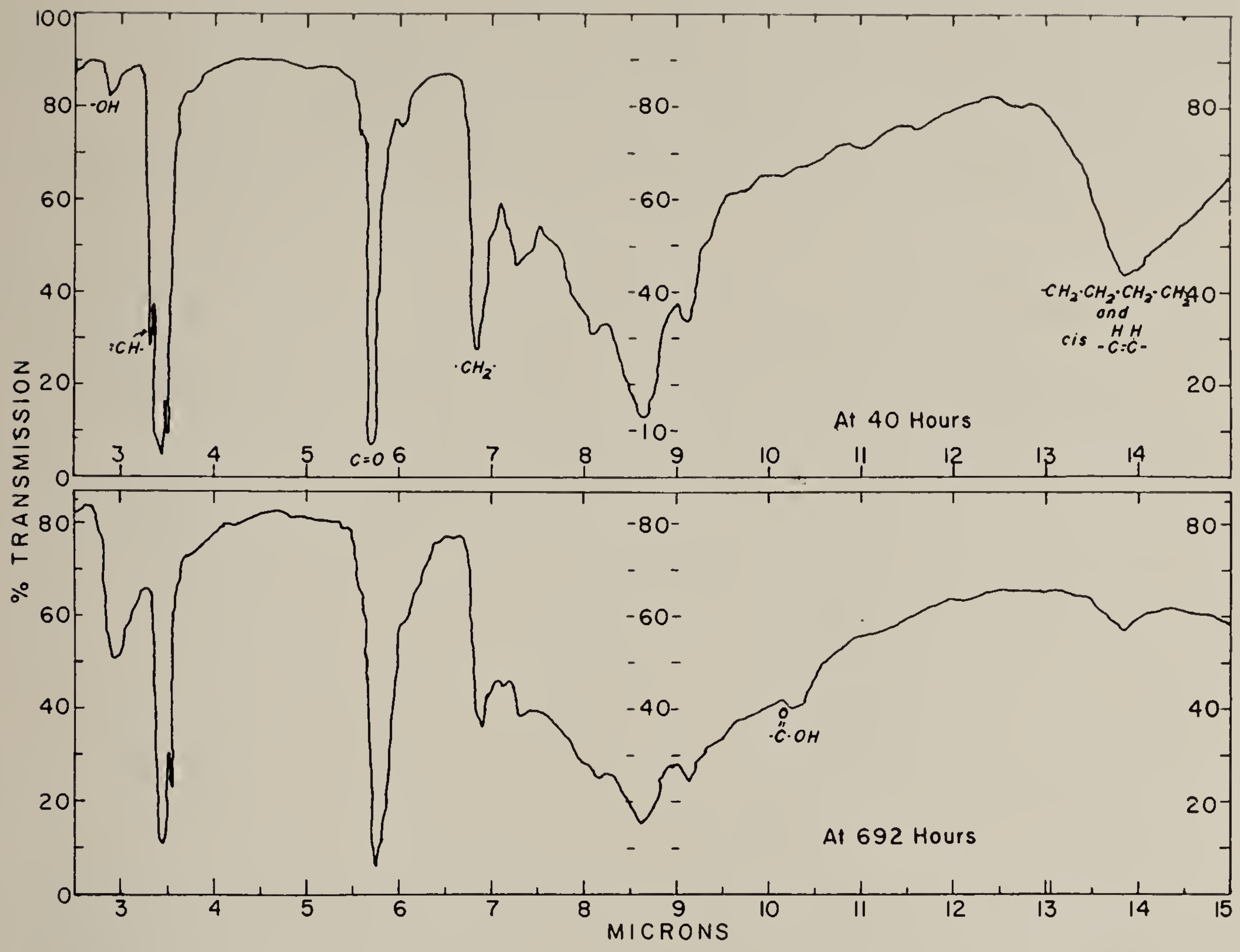


Fig. V-16. Infrared spectra of varnish linseed oil at 40 and 692 hours.

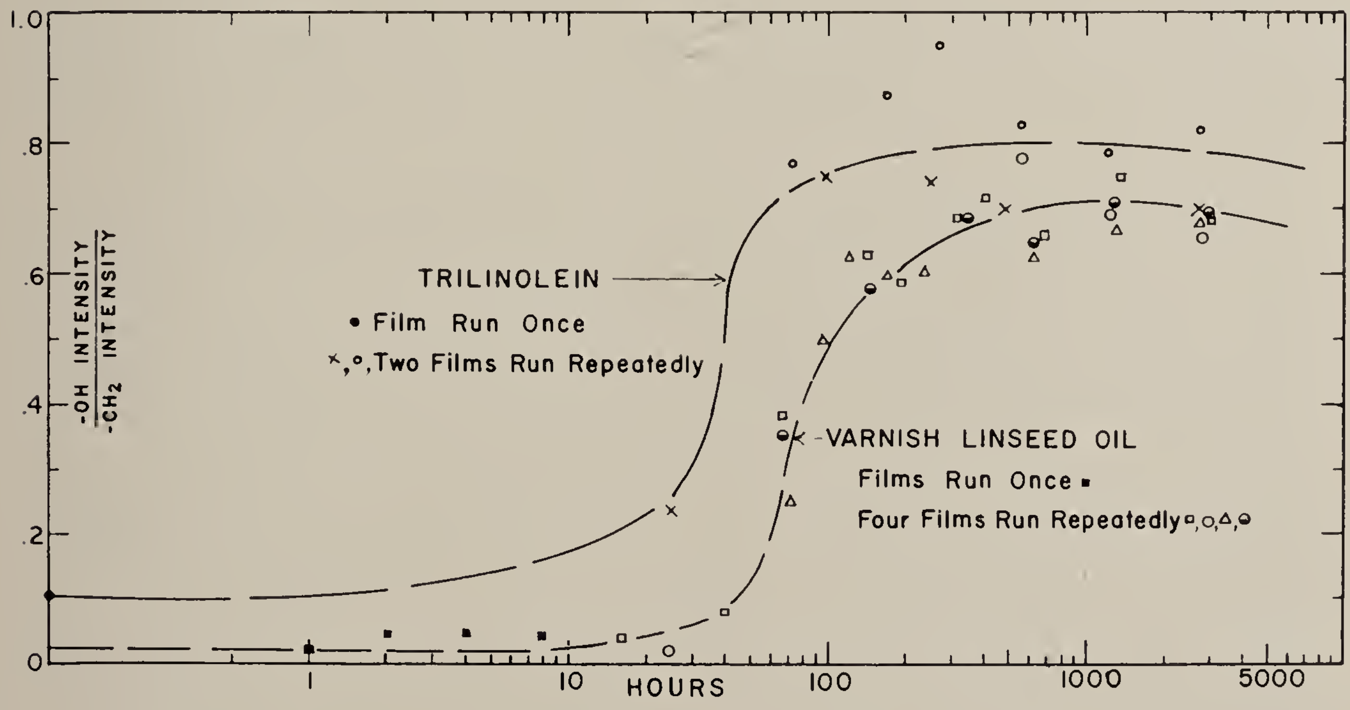


Fig. V-17. Changes in the infrared —OH absorption band of trilinolein and linseed oil films on drying.

leaving a thinner area at the central portion where the infrared beam falls. In Tables V-1 and V-2 are shown comparisons of the —OH and —CH_2— bands in varnish linseed oil and trilinolein, and they are plotted against time in Fig. V-17. Oxidation is seen to proceed

TABLE V-1

Rate of Oxidation of Films of Varnish Linseed Oil as Indicated by the Change in the Infrared —OH Absorption Band

—OH Intensity/—CH_2— Intensity = $\Delta d(2.88\text{–}2.70\ \mu)/\Delta d(6.83\text{–}6.50\ \mu)$

Column *A:* Films scanned once and discarded.

Columns *B–E:* Four films which were scanned repeatedly.

Age (hr.)	*A*	*B*	*C*	*D*	*E*
0	.022				
1	.023				
2	.041				
4	.043				
8	.045				
16		.043			
24	.021, .028		.021		
40		.081			
48	.092				
65.5					.35
67		.38			
72				.25	
96				.50	
120				.63	
144		.63			.58
166.5				.60	
192		.59			
236				.61	
309.5		.69			
336					.69
407		.72			
556			.78		
620					.65
621.5				.63	
692		.66			
1208			.69		
1273					.71
1274				.67	
1345		.75			
2761.5			.65		
2826.5					.70
2828				.68	
2898		.68			

TABLE V-2

Rate of Oxidation of Films of Trilinolein as Indicated by the Change in the Infrared —OH Absorption Band

$—OH\ intensity/—CH_2—\ intensity = \Delta d(2.88–2.70\mu)/\Delta d(6.83–6.50\ \mu)$

Column *A:* Film scanned once and discarded.

Columns *B* and *C:* Two films which were run repeatedly.

Age (hr.)	*A*	*B*	*C*
0	.11		
24.5		.24	
72			.77
96.5		.75	
168			.87
260		.74	
268.5			.95
479.5		.70	
557.5			.83
1131		.77	
1206			.79
2685.5		.70	
2760.5			.82

slowly in the linseed oil film for the first 24 to 30 hours, but then rises sharply until it reaches a nearly constant ratio of —OH to $—CH_2—$ absorption at about 150 hours; there was only a slight further increase to an age of about 2800 hours. Trilinolein oxidizes faster, but in a very similar manner. The fact that the intensity of the —OH band does not decrease, in spite of the probable decomposition of hydroperoxides with age, is evidence that alcohols as well as aldehydes and acids are present as residual products of oxidation.

Infrared Spectra, Project 6—McGill University

Dr. R. V. V. Nicholls and W. H. Hoffman used a Beckman Model IR-1 infrared spectrophotometer designed for routine hydrocarbon analysis, and loaned for this study by Shell Oil Co. of Canada, Ltd. It has been fully described by Brattain *et al.* (13,14). It had no facilities for the examination of liquid samples or solid films, but a liquid absorption cell and cell holder were made from specifications supplied by its manufacturer. It was set up in a room in which the relative humidity was kept close to 50% by air-conditioning equipment provided by the Canadian Paint, Varnish and Lacquer Association.

Since this spectrophotometer was not equipped with a wavelength drive nor automatic recording attachment, measurements were made point by point, using cell in–cell out technique to obtain per cent transmission values. This technique consisted of taking an energy reading x by galvanometer deflection with the cell in the optical path, then removing the cell and taking another reading y. Per cent transmission $= 100\ x/y$. This technique automatically eliminates peaks due to vapors in the atmosphere, chiefly water and carbon dioxide; all absorption maxima are due to the sample itself. For strict accuracy a pair of perfectly matched cells should be used and the full cell replaced by the empty one; however, rock salt absorbs so little energy in this spectral region that for the purposes of this study deviations are negligible.

The resolving power of the instrument permitted detection of all peaks, using an interval of 0.05 μ in taking transmission values. This interval was used in the regions of maximum absorption, but to speed up the readings the interval was increased to 0.10 μ in all other regions. Each spectrum reading took from 1 to 3 hours, depending on the range scanned. Slit width across the spectrum was varied according to the galvanometer deflection obtained; it was increased where necessary to insure accuracy. Where comparisons were made of the heights of peaks, the slit-width variations were carried out at the same wavelengths, and the widths were adjusted to an identical set of values for all spectra, to insure strict comparability of transmission percentages.

The materials investigated were: pentaerythritol esters of linseed fatty acids, trilinolein, PE linoleate, blown linseed oil (O viscosity), and heat-bodied linseed oil (L viscosity). The latter two were commercial products kindly supplied by Canada Linseed Oil Mills, Ltd. Films of all of these were dried at three different temperatures: 25°, 110°, and 175° C. In each series, several films of the vehicle were laid and placed in an oven under appropriate conditions. They were then removed successively after varying intervals and the spectra read. It was impractical to make successive readings on the same film during the early stages of the drying process, for two reasons. First, the films were examined in vertical position and thus, while still liquid, they would flow if uncovered. Second, because of the time required for a reading, it was necessary to cover the film to retard oxidation while in the instrument. If the film was not touch-dry, it was ruined for further readings when the rock-salt covering plate was removed.

The films were cast on polished rock-salt plates with the aid of a three-sided spacer of aluminum foil, 0.03 mm. thick. Three or four drops of oil were placed in the central area, and another rock-salt plate pressed down, forcing the excess liquid out at the open side. The top plate was slid off toward that side leaving, on removal of the spacer, a film approximately 0.03 mm. thick on the bottom plate.

As in the studies just described, most films were cast without addition of drier to the vehicles; however, in this case a few with drier were also studied, an aging period of 24 hours after its addition being observed. All films were dried in the dark.

Experimental

The spectra (from 2.5 to 15 μ) of films of the PE esters of linseed acids, dried at 25° C. and 50% relative humidity for the periods shown at the side of each curve, are plotted in Fig. V-18. That of the original compound exhibits absorption maxima at 3.45, 5.75, 6.85, 7.10, 8.00, 8.45, 9.70, 10.80, and 11.50 μ. The band at 3.45 μ is caused

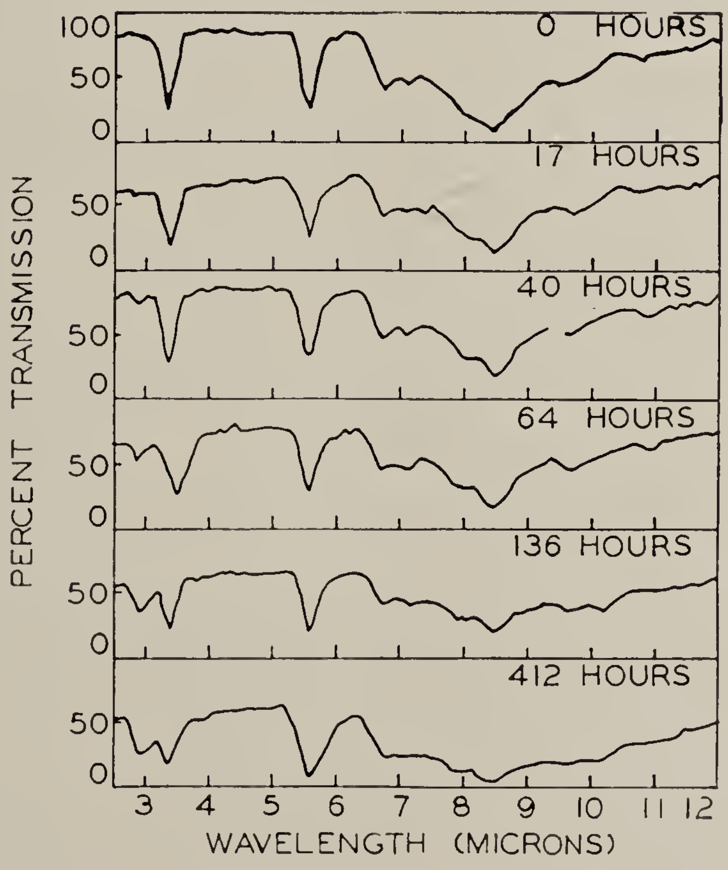


Fig. V-18. Infrared spectra of PE esters of linseed fatty acids, dried in darkness at 25° C.

by stretching vibrations of C-H bonds, that at 5.75 μ by the carbonyl group, that at 6.85 μ by the methylene bending (4,63). Thompson (63) believes the band at 7.10 μ points to a terminal methyl group, Cherrier (17) to methylene bending; either possibility would be reasonable. The prominent band at 8.45 μ and the poorly resolved one at 7.90 to 8.00 μ are characteristic of a $>C{=}O$ group where the carbon is unsaturated, as in the ester or carboxyl groups (48). The band at 9.70 μ appears to be due to a pentaerythritol skeletal vibration; it is absent from the spectra of glyceryl esters but present in that of PE linoleate. Ethylenic linkages in the carbon chains are probably responsible for the bands at 10.80 and 11.50 μ, and the —C=C— vibration may show up in the indistinct band at 6.10 μ.

The most noticeable change in the later spectra is the appearance and growth of the band at 2.90 μ ascribed to the hydroxyl group, undoubtedly including both —OH and —O—OH vibrations; Shreve *et al.* (57) find no appreciable difference in their stretching frequency, but Dugan and coworkers (21), studying the oxidation of methyl linoleate, distinguished a band at 2.91 μ as due to hydroperoxide and one at 2.88 μ as due to alcoholic OH. The instrument at Montreal could not resolve these two bands.

The carbonyl band at 5.75 μ also increased in intensity, and that at 7.90 to 8.00 μ grew and became more complex; after 136 hours, it split into two persistent bands. This behavior may indicate increased concentration of ester groups (49), although the band at 8.45 μ also considered characteristic of esters showed no comparable change.

A band at 11.50 μ in the spectrum of the original oil persisted through most of the later ones; those of the exposed films contained new bands in the region from 11.60 to 11.80 μ, possibly indicating formation of epoxides. However, Shreve *et al.* (57) believe that bands of somewhat variable frequency in the 10- to 12-μ range stem from hydroperoxides.

Sixty-four hours brought out a persistent band at 9.20 μ attributed to ester groups (62), ether linkages (63), or secondary hydroxyl bending (2,54), which last seems most likely. An ethylenic linkage of *trans* configuration (52,39) may have caused a band at 10.10 to 10.20 μ which appeared and remained after 136 hours—apparently a consequence of shift and concomitant inversion of double bonds from *cis* to *trans* during autoxidation (45,34).

Drying of the film, with its general increase in absorption over the region upward from 6.5 μ, leveled out many of the peaks. Oxidation of the oil may have introduced many new types of bonds with absorption maxima in this region, not resolvable by the spectrophotometer. The curve forms an ill-defined plateau, similar to that found by Jones (37) in studies of fatty acid metabolism.

Effect of Temperature

In the studies of films of these same PE esters of linseed acids at higher temperature, emphasis was on changes in the hydroxyl and carbonyl peaks; accordingly, except in one or two cases, readings were made only up to 6.5 μ. Figure V-19 shows representative spectra of films dried at 110° and 175° C., respectively. They differ very little from the 25° C. series. After a quarter-hour at 175° C., when the oil had nearly set to touch, no peak at 9.10 μ had appeared. No subsequent reading in this region was made; but for films dried at 25° and 110° C. such a peak was evident even while the film was still fairly wet, so it is not likely that it would have been found at 175° C. This indicates a difference in the drying mechanism at this higher temperature and points to the possibility that vinyl or Diels-Alder polymerization takes a prominent role.

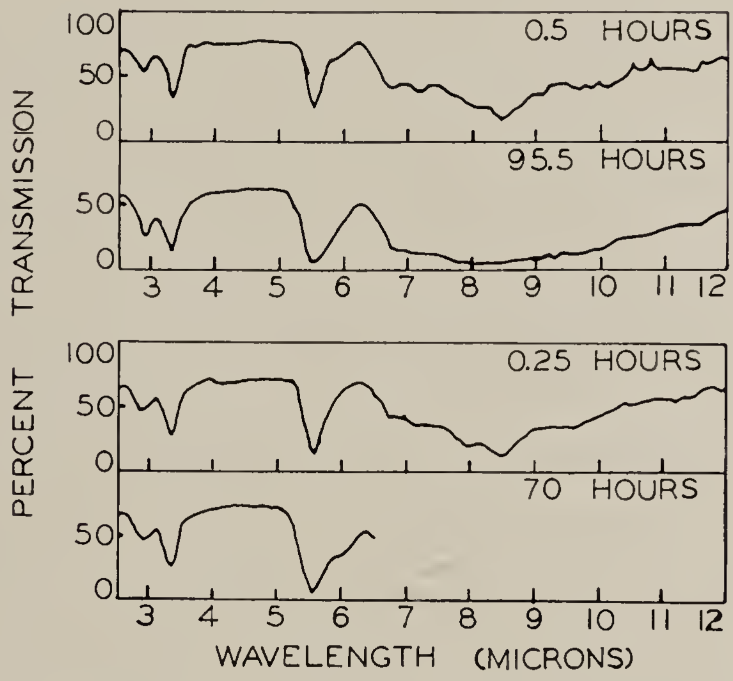


Fig. V-19. Infrared spectra of PE esters of linseed fatty acids, dried in darkness at 110° C. (above) and 175° C. (below).

Another influence of higher drying temperatures appeared in the carbonyl band at 5.75 μ, which widened toward longer wavelengths. At 110° C., 28 hours was needed to develop this noticeably; at 175° C., 9 hours was enough, and beyond 70 hours a new peak at 6.05 to 6.20 μ was detectable. Groups responsible for this may also have imparted the deep amber color of the film. A ketonic carbonyl group in conjugation with a —C=C— double bond is reported (53,63) to give rise to carbonyl absorption at 5.90 to 6.00 μ and to a double-bond absorption at 6.07 to 6.17 μ. The peak detected in these studies might have been due to poor resolution of these maxima. Ultraviolet absorption spectra have indicated (6,10,43) the probability of such arrangements of functional groups.

Effect of Driers

To assure comparability of results, the PE-linseed acid ester was again used in these tests. In one series, the Federation drier was added; in another, 0.025% cobalt alone; in the third, 0.03% lead alone. All driers were naphthenates, and all mixtures were aged 24 hours before laying films. As before, films were dried at 25° C. and 50% relative humidity.

The most extensive study was made of the oil with combination drier (Fig. V-20). Comparison with Fig. V-18 shows several differences between the unexposed, aged oil with drier and that with no drier. A slight hydroxyl absorption appeared at 2.90 μ. Although the oil had been aged under nitrogen, enough oxygen may have been present in solution in it to permit some oxidation under the stimulation of the drier. The peak at 7.90 μ was more pronounced and peaks at 11.65 and 11.85 μ (possibly, as discussed above, due to epoxides) appeared. The changes observed during the course of drying were the same as for films without drier.

The films containing cobalt drier alone, and lead alone, yielded spectra similar to those of the films with the combination drier. Likewise, the spectra of films of trilinolein and PE linoleate (Fig. V-21) and those of the two commercial linseed oils differed in no noticeable respect from those of the PE-linseed acid esters.

Changes in Hydroxyl and Carbonyl Absorption Maxima

Quantitative changes in intensity of the peaks at 2.90 and 5.75 μ, respectively, were arrived at by using the same procedure as was

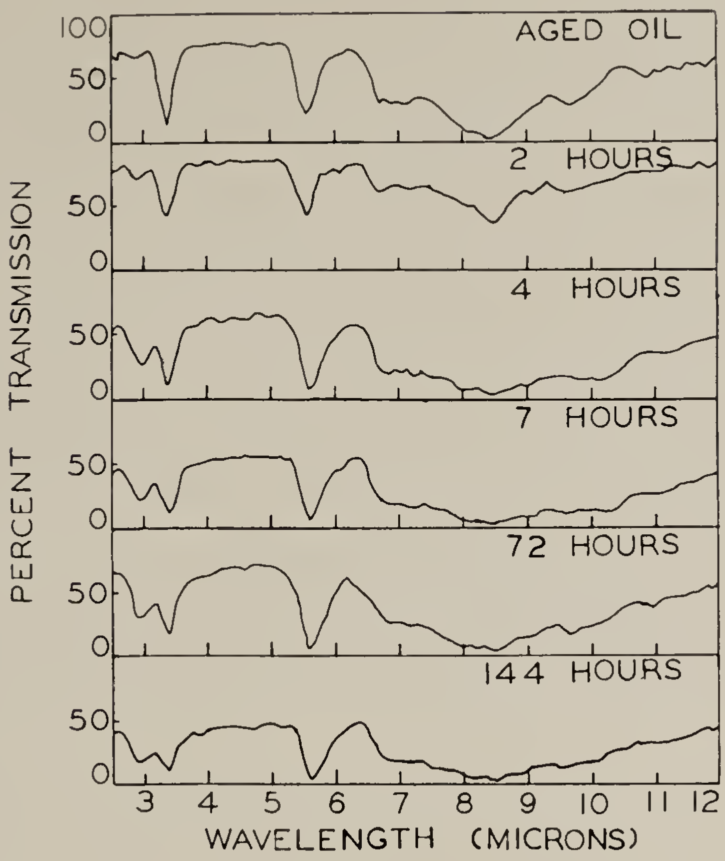


Fig. V-20. Infrared spectra of PE esters of linseed fatty acids, with Federation drier added; dried at 25° C.

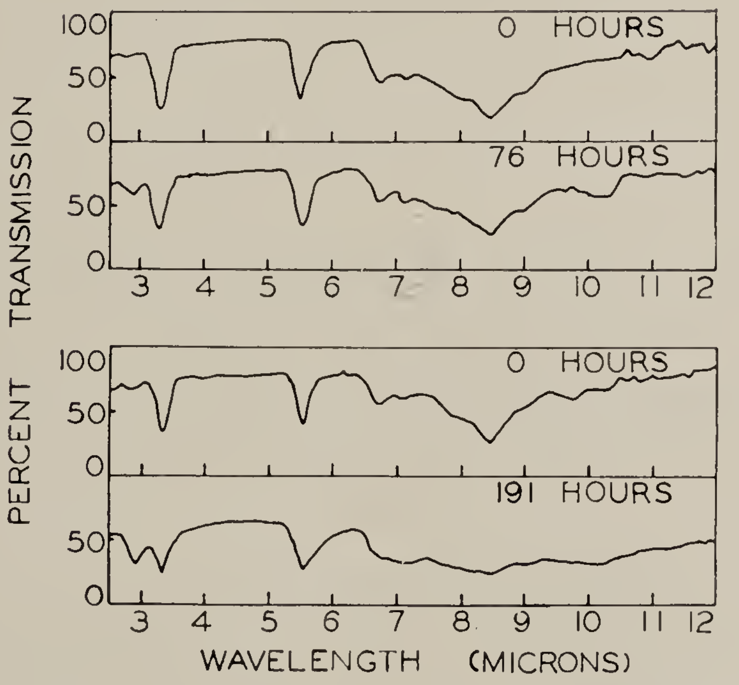


Fig. V-21. Infrared spectra of trilinolein (above) and PE linoleate (below), dried in darkness at 25° C.

followed by the New England Club cooperators. The optical density values for these hydroxyl and carbonyl bands were divided by that of the carbon-hydrogen band to reduce all readings to a comparable scale.

It was observed that the minima in the various spectra lie along a base line which is not straight but varies in slope through the range of readings. Further, the distance between this base line and 100% transmission varies from spectrum to spectrum, probably owing to imperfections on the film surfaces which give rise to different degrees of scattering of the radiation striking the film. To correct for this variation and thus reduce different spectra to a comparable state, the method of base line optical densities (32) was employed. In this method the base line is drawn on the spectrogram and optical densities are calculated in the normal manner. Thus I_0, instead of being 100, becomes the distance from zero per cent transmission to the base line, at the frequency of the absorption peak. The value of I is, as usual, the distance from zero per cent transmission to the top of the peak.

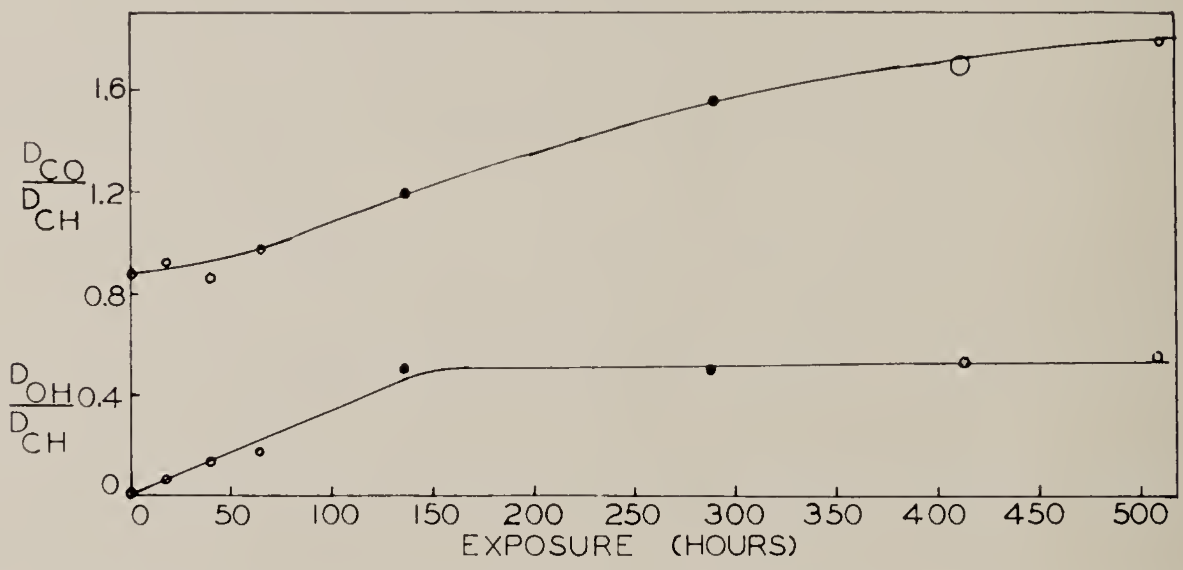


Fig. V-22. Changes in concentrations of carbonyl and hydroxyl compounds (as measured by optical densities) of drying films of PE esters of linseed fatty acids.

Values of the optical density of the hydroxyl peak divided by that of the carbon-hydrogen peak, and similarly of that of the carbonyl peak divided by the same divisor, were figured in this manner and plotted against time. In the interest of brevity, only a few representative curves are shown, in Figs. V-22 to V-25. In each graph, two of the circles representing experimentally determined points are blackened. The oil set to touch in the interval between these blackened points. Large circles indicate points where experimental accuracy is low.

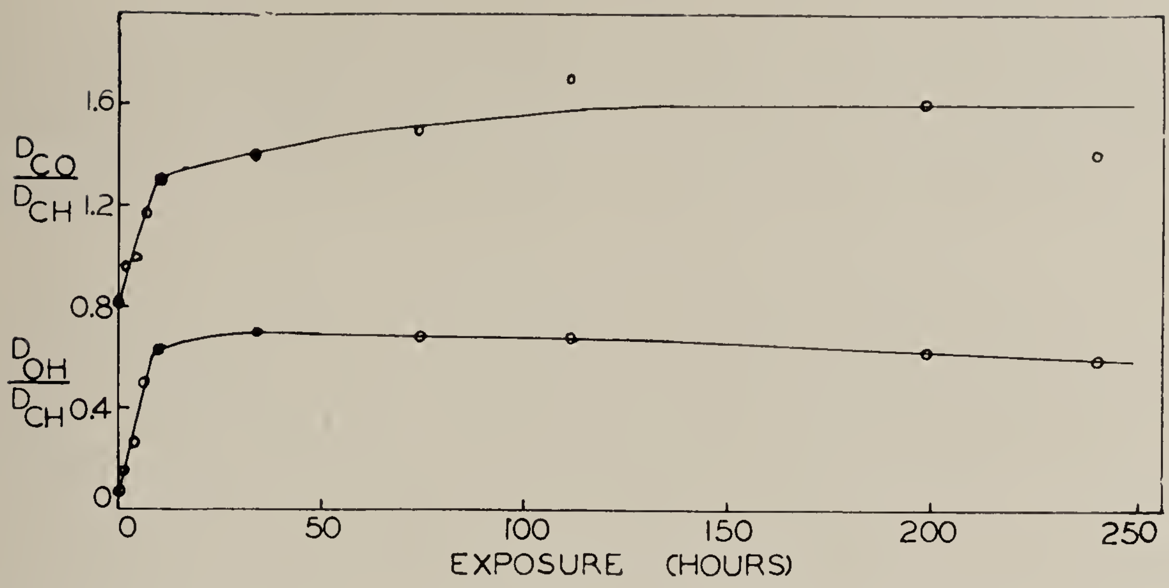


Fig. V-23. Changes in concentrations of carbonyl and hydroxyl compounds (as measured by optical densities) of drying films of PE esters of linseed fatty acids containing 0.025% cobalt.

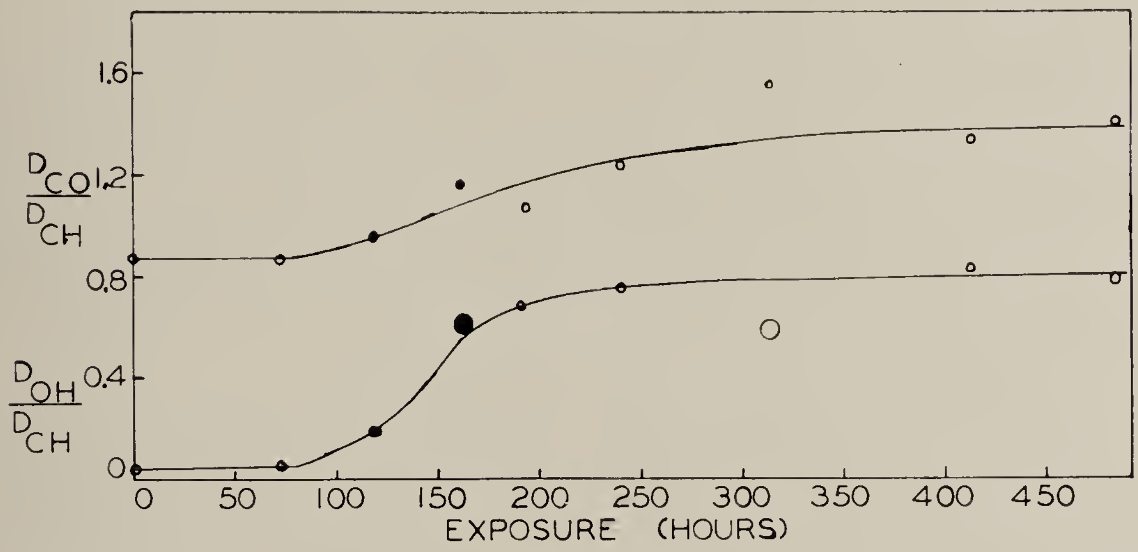


Fig. V-24. Changes in concentrations of carbonyl and hydroxyl compounds (as measured by optical densities) of drying films of PE linoleate.

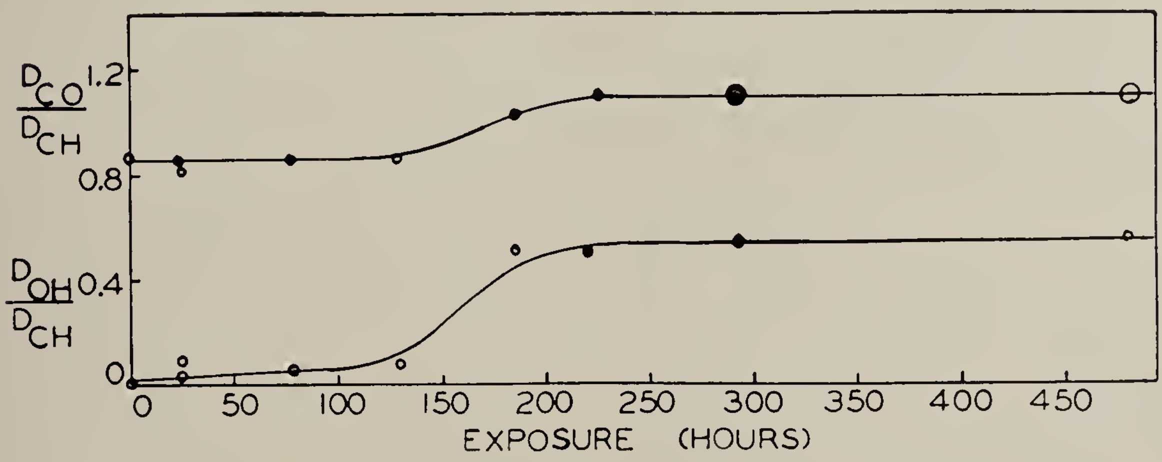


Fig. V-25. Changes in concentrations of carbonyl and hydroxyl compounds (as measured by optical densities) of drying films of L-bodied linseed oil.

In spite of the many assumptions and approximations on which this method is based, the fact that the points, each representing a separate film, lie on relatively smooth curves is a good check not only on individual determinations but on the method of computation as well.

For the PE-linseed acid ester, the curves have, in general, two distinct portions divided by a reasonably sharp region of change. Hydroxyl concentration increases rather rapidly at first, then remains fairly constant (at 0.55 for films dried at 25° C.). This maximum region varies with different oils, from a slight upward to a slight downward slope. The set-to-touch point comes in most cases at about the region of discontinuity. For the carbonyl concentration curves the change in slope usually comes later and is less abrupt. Thus in Fig. V-22 this change is gradual throughout and does not reach a maximum within the period investigated.

At higher temperatures the maximum values are reached much sooner; that of hydroxyl concentration at 0.50 after 45 minutes at 110° C., and at 0.36 after only 10 minutes at 175° C. Sharp discontinuity came sooner also in the carbonyl curve at 175° C., but it was still on an upward slope at 2.6 when last measured, as compared with the maximum of 2.1 at 110° C. and highest reading (still trending higher) of 1.8 at 25° C.

As would be expected, driers speed the attainment of maxima. Most effective is the cobalt-lead combination, with cobalt alone a close second, lead a poor third. With cobalt alone (Fig. V-23), the hydroxyl concentration falls off after reaching its maximum, probably signifying increased oxidation of hydroxyl groups to ketones; carbonyl increases somewhat, but its maximum comes later than that of hydroxyl.

The maximum values reached by the two concentration curves for films with and without drier are as follows:

Drier	Hydroxyl concentration	Carbonyl concentration
None	0.55	1.8 (at last reading)
Cobalt-lead	0.62	1.9
Cobalt	0.65	1.6
Lead	0.63	1.5

Addition of drier appears to raise the height of the maximum for hydroxyl, with no great difference between the different drier dosages. For carboxyl the combination drier had little effect, but with either metal alone the maximum is lower—an opposite effect to that of higher temperature, indicating an appreciably different mechanism of drying.

Synthetic Linoleates

Both the glyceryl and PE linoleates displayed apparent induction periods of approximately 75 hours in their curves. In view of the care taken in purifying the fatty acid, this might be considered surprising; however, it is perhaps explainable in part by the autocatalytic nature of peroxide formation, by the multiplication of hydroxyl and carbonyl compounds through degradation of the peroxides, and by other secondary oxidation reactions. Both samples, when read immediately upon opening the vials in which they were received, showed hydroxyl peaks, indicating the presence of a slight excess of the esterifying polyalcohol. Another peculiarity shown by these compounds was that the maximum hydroxyl value for the PE ester, though reached later, was 0.80 as compared with 0.50 for the glyceryl ester. The respective carbonyl concentration maxima were more nearly alike, 1.35 and 1.43.

Processed Linseed Oils

Induction periods in the curves for these are to be expected; that for the heat-bodied oil (Fig. V-25) is quite long. Antioxidants in the blown oil were partially destroyed by the oxidation, so that the induction period was shortened. Both oils have the same maximum (0.58) for their hydroxyl curves, but the carbonyl maximum is 1.10 for the heat-bodied and 1.60 for the blown oil; the reduction of the number of double bonds by previous polymerization apparently decreases the amount of carbonyl compounds that may be formed. In contrast, high-temperature oxidation decreases the hydroxyl maximum but increases the carbonyl maximum.

Although, as just mentioned, the lower carbonyl maximum for the heat-bodied oil can be accounted for by the reduction in unsaturation due to its prior polymerization, a lower hydroxyl maximum would also be expected. Perhaps hydroxyl and carbonyl groups are formed at distinctly different positions on the fatty acid chain. Heat-bodying might reduce the number of those linkages where carbonyl compounds are formed, but not of the others. By the same reasoning, the increased carbonyl and reduced hydroxyl maxima for oils dried at high temperature point to different linkages for polymerization reactions in the two cases. A relation seems likely between this finding and the differences noted in the "gain in weight" project between the behavior of air-dried and baked films.

Infrared Spectra, Project 24—The Hormel Institute

As a part of a broad study of oxidation changes by Chipault and McMeans at The Hormel Institute, infrared spectra were read of liquid films of fatty acids derived from two pure esters (trilinolein and trilinolenin) at two stages of drying. The method of preparation of these acids is described in the fuller discussion of Project 24 in Chapter XIII, but results are reported here for comparison with the other infrared studies.

The instrument used was a Perkin-Elmer Model 21 double-beam spectrophotometer, and Fig. V-26 presents the curves obtained. The fatty acids from the films of both trilinolein and trilinolenin, at the "slightly tacky" and "tack-free" stages, are generally more opaque in the 6- to 12-μ region than the corresponding unoxidized acids. With both compounds, there is no noticeable difference between the spectra of the fatty acids obtained from the tacky and tack-free films. All

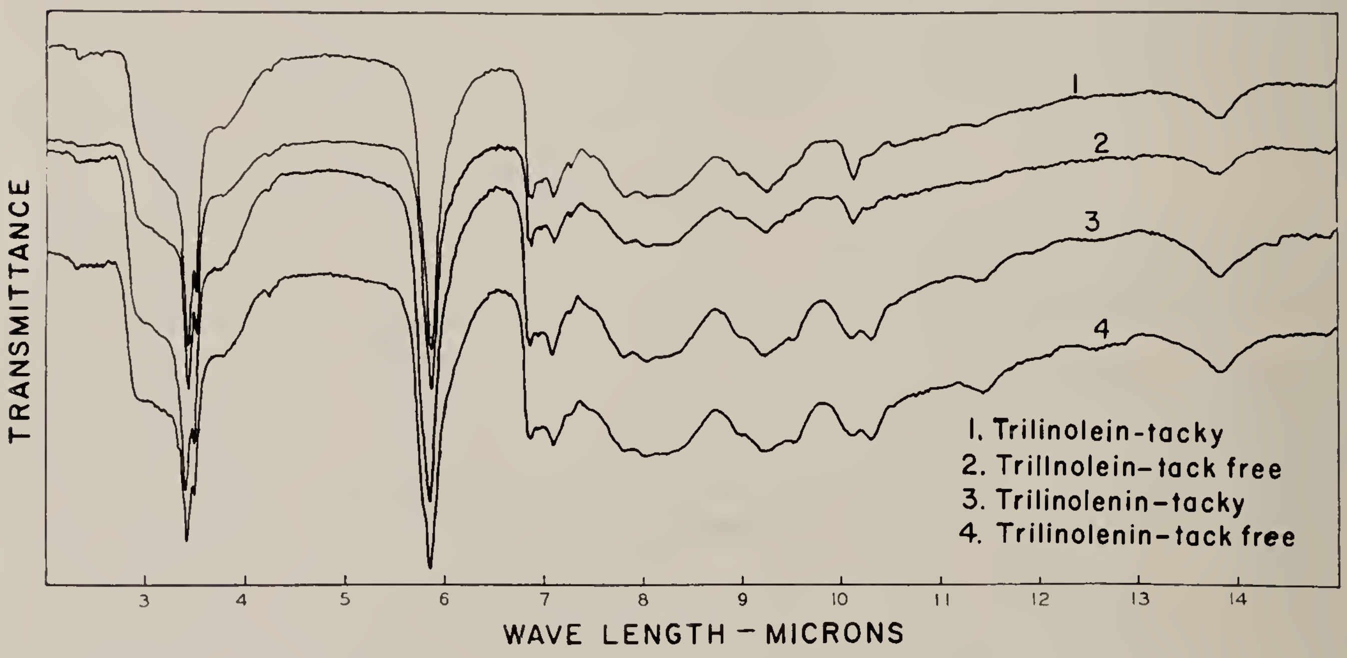


Fig. V-26. Infrared spectra of fatty acids from "tacky" and "tack-free" films of trilinolein and trilinolenin.

the curves show a broad absorption band between 2.8 and 3.2 μ which merges with the C—H stretching absorption at 3.4 μ. The intensity of this band indicates that considerable amounts of OH groups other than those of carboxyl are present. The base of the carbonyl band at 5.85 μ is broader than that for the unoxidized acids, probably because of other carbonyl compounds formed. A broad weak band at 9.24 μ and a weak band or inflection at 8.95 μ may be due to the secondary OH groups of the reduced hydroperoxides or to ketonic compounds.

General Discussion of Infrared Data

Farmer (25) and others (8,41) reasoned that the first step in the autoxidation of drying oils is the formation of hydroperoxide on the carbon adjacent to a double bond, and that this and other reactions reduce the unsaturation. (However, Farmer (24) more recently supported the Gunstone and Hilditch (29,30) view that the original entrance of oxygen might be at a double bond.) The spectral changes give evidence for both these mechanisms; and their correspondence with drying rates is indicated by the curves (Fig. V-27) showing the per cent transmission for the 2.8-μ region as a function of time exposure for the first week or more. Readings made, in some cases, at intervals over several thousand hours confirm the indication of these curves that transmission approaches and maintains a reasonably constant value. Figure V-28 plots per cent absorption against time in both the 2.78-μ and the 3.27-μ regions for the diPE linoleate and linolenate. The hydroperoxide absorption increases whereas that of the methylenic —CH— decreases proportionately.

The 8.0-μ region band may be due in part to epoxide linkages; epoxides are postulated by several workers (11,23,26–28,54,56) as decomposition products of hydroperoxides, with bands in this area, and epoxide derivatives of monounsaturated fatty acids exhibit, in addition, a band at 11.8 to 12 μ for *cis* isomers, at 11.2 to 11.4 μ for *trans*.

The fact that the relative optical density of the carbonyl absorption approximately doubled during the drying process suggests that in this oxidation the oil, originally containing one carbonyl group per fatty acid residue, gains an additional one. The changes in hydroperoxide concentration are not so easy to follow, since its

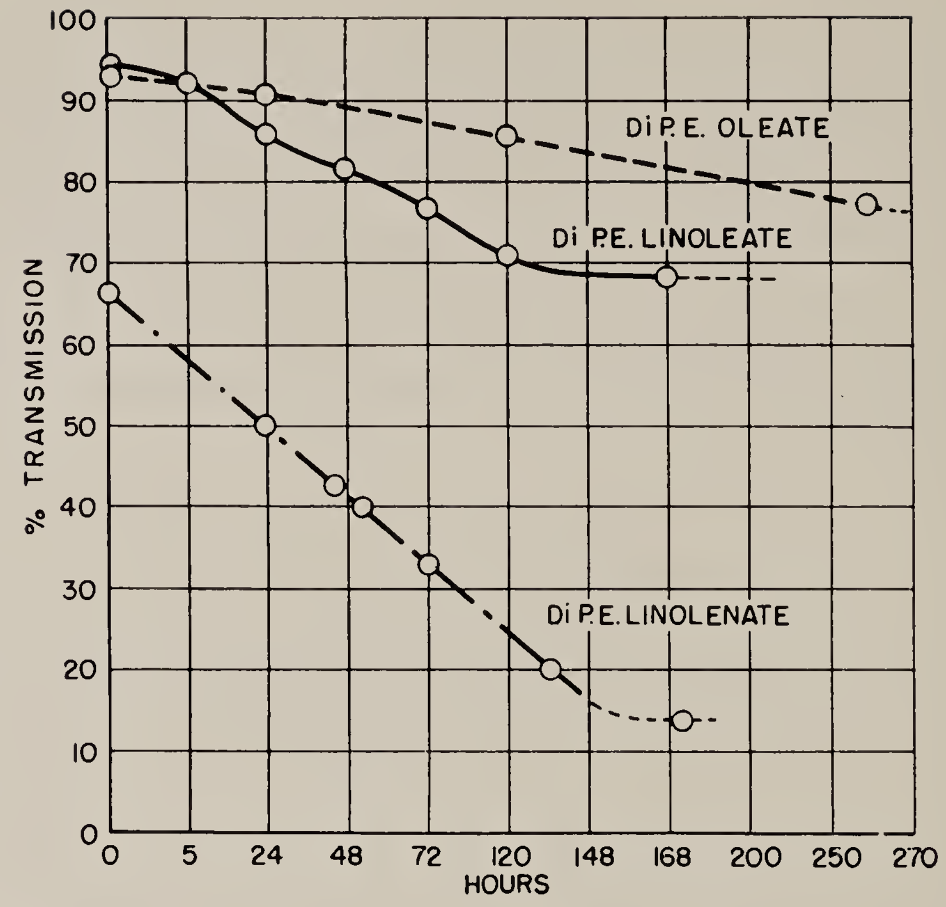


Fig. V-27. Changes in concentration of hydroperoxide (as measured by transmission at 2.78 to 2.82 μ) of drying films of diPE oleate, linoleate, and linolenate.

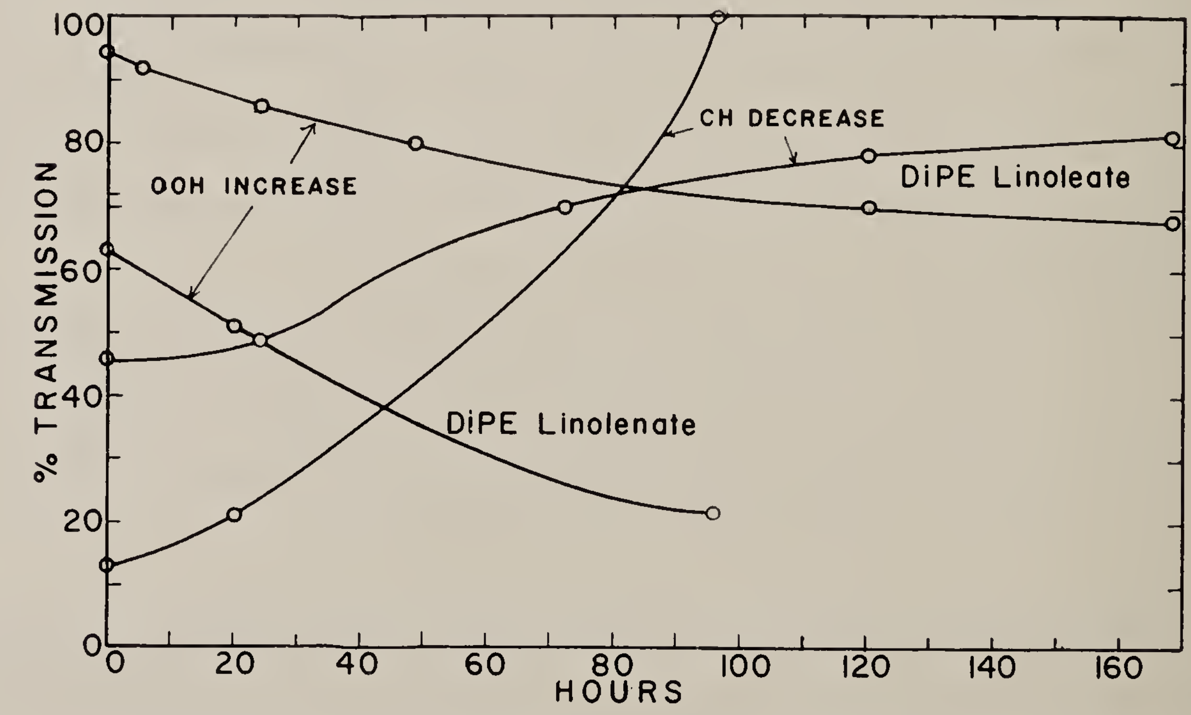


Fig. V-28. Changes in concentration of hydroperoxide and methylenic CH (as measured by transmission at 2.78 and 3.27 μ) of drying films of diPE linoleate and linolenate.

absorption bands are included in overall hydroxyl absorption. On the assumption that a similar mechanism is operative to that found by Honn, Bezman, and Daubert (34) in the case of autoxidation of raw linseed oil in bulk, it is likely that initially, at least, most if not all of the hydroxyl absorption is due to hydroperoxides, which then decompose to yield hydroxyl and carbonyl compounds plus some polymers. Increase in carbonyl concentration even after the film has set, when the chance of oxidation except at the surface is slight, indicates that it comes from oxygen-containing compounds already present in the film. Dehydration of hydroperoxides, a possible source, would cause a decrease in hydroxyl concentration which does not occur; however, epoxides, if present, could rearrange to form ketones without reducing hydroxyl content.

Shreve *et al.* (55) have shown that the isolated *trans* double bond absorbs at 10.35 μ. Jackson *et al.* (36) found a strong band at 10.12 μ characteristic of conjugated *trans, trans* diene whereas conjugated *cis, trans* diene showed a doublet at 10.18 and 10.52 μ. For the trilinolein fatty acids examined by Chipault and McMeans the peak at 10.12 μ and the slight inflections at 10.32 and 10.52 μ indicate the presence of appreciable amounts of *trans, trans* conjugated diene with minor quantities of conjugated *cis, trans* diene and isolated *trans* unsaturation.

In the case of the trilinolenin acids, the strong peaks at 10.12 and 10.32 μ betoken both conjugated *trans, trans* diene, and isolated *trans* unsaturation; the lack of absorption at 10.52 μ indicates the absence of conjugated *cis, trans* diene. The weak peaks at 9.52 and 11.42 μ may be due to aldehydic or oxirane groups.

Evaluation of Infrared Results

Although four different groups worked in the field of infrared spectrometry, so much effort was required by each in the development of special techniques that only a few of the pure compounds were examined and the fragmentary data do not lend themselves to close correlation with the other projects. Dr. D. H. Wheeler offers the following comments.

The Oxygen-Hydrogen Bands at 2.8 to 2.9 Microns

During the drying of films of diPE esters of oleic, linoleic, and linolenic acids, Adams, Auxier, and Wilson found (page 116) that a band attributed to OOH or OH groups appeared at about 2.8 μ and increased in intensity with time, at a rate proportional to their known relative rates of oxidation. Similar —OH bands were observed by the McGill University and Hormel Institute teams and by others (21,34,40) in drying oils and esters autoxidized under other conditions, as well as in pure fatty hydroperoxides and their hydroxylic reduction products (50,51). Whereas both the pure hydroperoxide and the derived hydroxy compound exhibit a strong band due to hydrogen-bonded dimer, on dilution this band becomes very weak, and a new band, due to unbonded OH or OOH, appears at about 0.1 μ shorter wavelength (31). Since the infrared bands of bonded and unbonded OH and OOH are all at only slightly differing wavelengths, and their tendency to become bonded differs, any quantitative measurements of OH and OOH by infrared are practically impossible when both are present.

The Carbon-Hydrogen Band at 3.3 Microns

The band at about 3.3 μ, which was strongest in linolenate, less in linoleate, least in oleate, and absent in stearate, was ascribed to a C—H stretching frequency of a CH_2 adjacent to a double bond. Its weakening with time was attributed to the attack, during autoxidation, of these active methylenes, with replacement of hydrogens by OOH groups. Later studies have shown that this 3.3 μ band is characteristic of *cis* double bonds which are not conjugated. Elaidic and linolaidic esters show only a very weak band, much weaker than oleate; conjugated diene esters show bands about as strong as oleate (31). Pure conjugated linoleate hydroperoxides derived from normal linoleate have a very weak band, much weaker than oleate or the conjugated linoleates (31,50). The decrease in this band can thus be explained by the shift to conjugation during hydroperoxide formation in the early stages of autoxidation, and undoubtedly by subsequent attack of the conjugated double bonds during further oxidation or decomposition of the peroxides.

Carbon-Hydrogen Bands at 10 to 11 Microns

Certain bands in the region from 10 to 11 μ are related to the frequencies of bending of hydrogen on double-bonded carbons. Isolated *trans* double bonds show a band at 10.3 μ, *trans, trans* conjugated dienes one at 10.12 μ, and *cis, trans* conjugated dienes a doublet at 10.18 and 10.54 μ (36). The studies of Chipault and McMeans show that *trans, trans* conjugated dienes are formed in the acids from trilinolein and trilinolenin at the stages of their readings. They observed a slight amount of isolated *trans* isomer present in the original debromination acids. Broadening of the acid carbonyl at 5.85 μ indicated formation of other carbonyl compounds without giving evidence as to their specific nature.

In addition to these specific bands, a general absorption in the region from 6 to 12 μ occurs as oxidation proceeds, probably related to a general or overlapping absorption of oxygenated compounds not as yet diagnosed.

Ultraviolet Spectra, Project 6c—McGill University

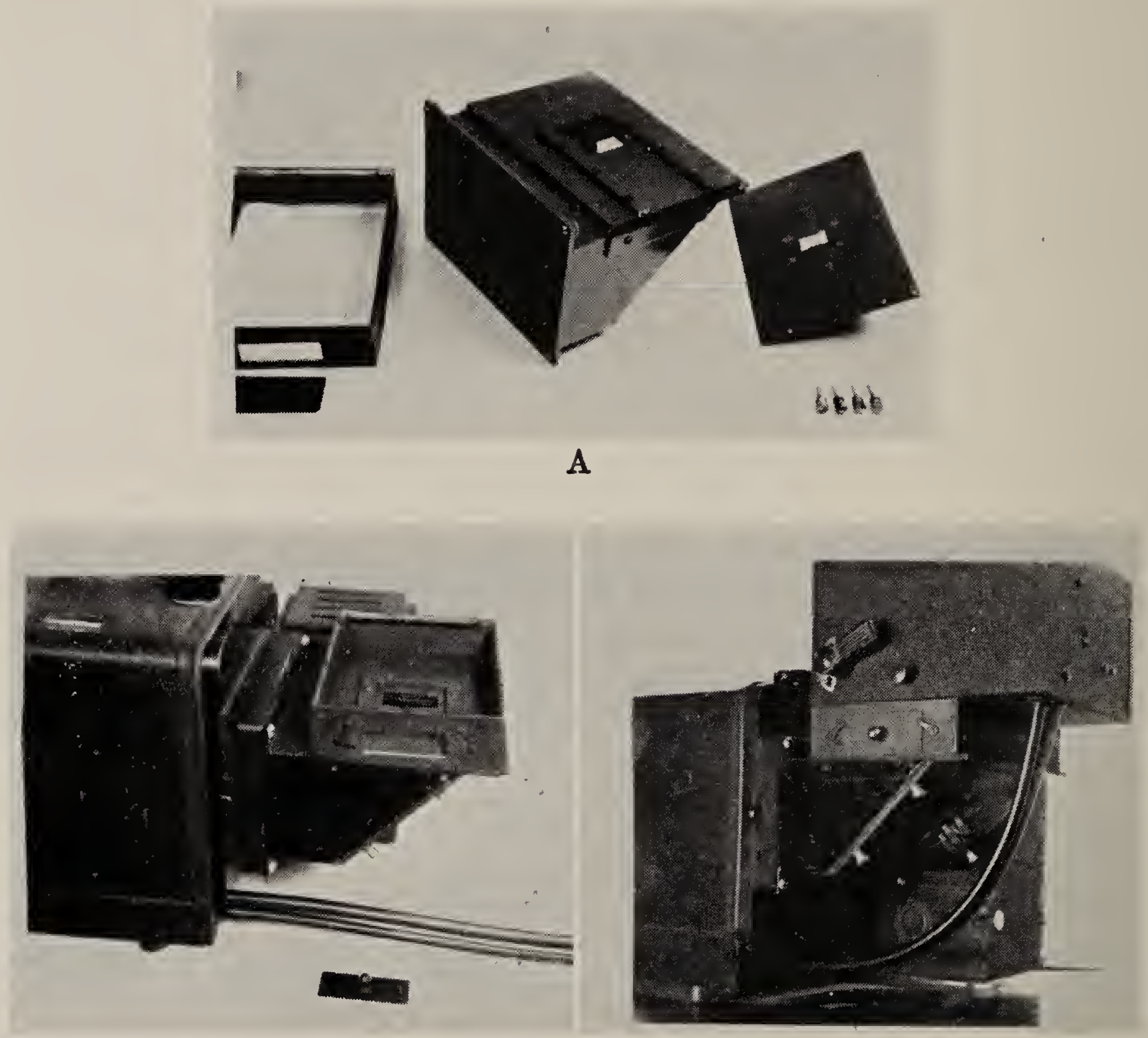
This study was undertaken by Dr. Nicholls at McGill with the help of graduate students H. G. McAdie and David Marshall. The report, written by McAdie and Nicholls, is presented here (with editorial changes) for the first time.

The original plan was to measure and interpret changes in light absorption during film drying and later deterioration over the range from 2000 to 10,000 Angstroms (200.0 to 1000.0 mμ) on all the Federation vehicles. Effects of variation in temperature, humidity, and light intensity during drying were also to be studied, and the work was to be repeated with controlled amounts of driers. Particular attention was to be given to the rise of chromophores in the visible range of the spectrum which are responsible for the phenomenon of yellowing. A number of obstacles which came up forced a considerable narrowing of the plan, the final accomplishment being examination of about a dozen Federation and commercial compounds in the UV region of 210.0 to 330.0 mμ under a single set of drying conditions.

Preparatory Work

The instrument used was a Beckman DU Quartz Spectrophotometer. Since this comes equipped with no means for taking readings on thin liquid films during their conversion to solids, the first problem was to design and build an attachment in which such films, to be cast on small quartz plates, could be placed in horizontal position at the point where the cell compartment would normally have been. A simple, inexpensive unit was developed.

This unit (Fig. V-29), attached to the spectrophotometer by four screws, had a round window fitting against the monochromator light exit window. The beam, passing through this, fell on a mirror of the same type as used in the monochromator and was reflected vertically upward through a small rectangular opening in a horizontal shelf. Guard rails on this shelf centered the quartz plate over this opening, and the beam, passing through, was focused on the phototube in its housing mounted above.


A

B

C

Fig. V-29. Holder for quartz plates carrying liquid films for UV spectrophotometer scanning. A, disassembled; B, mounted on instrument; C, with phototube housing in place.

An attempt was next made to devise a means for laying films of prescribed Federation thickness. The quartz plates were only 30 × 40 × 2 mm. in size, too small for the use of customary applicators in casting the films. A special doctor-blade apparatus was designed and built for this operation. A razor blade with edge free from flaws was mounted in a carrier which traveled in slots milled into supporting bars on either side, over a cast iron base provided with guide rails to position the silica plate just under the blade. Clearance between plate and blade could be accurately adjusted for any desired film thickness. A "T" pattern of oil was placed on the plate from a hypodermic syringe and the blade pulled over to spread the film, the excess oil escaping over the edge.

Another gadget was prepared for measuring accurately the thickness of the films thus laid. The plate on which the film had been cast was placed in a "Lucite" box $^1/_2$ mm. larger than the plate. The box had been filled with mercury to just below the top so that the plate floated level with its surface above the top edge of the box. Box and contents were placed on the stage of a microscope equipped with a micrometer screw, and with a steel sewing needle strapped to one of its objective lenses. With suitable illumination and optical system, readings were made as the needle point, slowly lowered, made contact first with the upper surface of the film and then with the plate itself.

A number of unsuccessful trials led to abandonment of the applicator described above in favor of a modified Spencer student microtome, which served fairly well for films about 1.25 mils (31 μ) thick. However, it was found that the optical density of films more than about 10 μ thick was too great for accurate measurement with this spectrophotometer; and further, that no matter how carefully the plates were cleaned, films laid with the microtome but without special precautions always crawled into discrete droplets. To prevent this, several types of undercoatings on the silica were tried. The most satisfactory was applied from a solution, 1% in xylene, of polyethylene ("Polythene") used at 80° to 90° C. Each plate was immersed in the hot solution, drained, baked in an oven at 120° C. for 5 to 10 minutes, and lightly polished. With care in cleaning and coating the plates, films of 30 μ or more in thickness could be prepared without too much difficulty. But months had elapsed during all this preparatory work; and to assure the gathering of as much information as possible with the least further delay, the quartz plates were finally abandoned. Instead, films were cast on strips of very thin lens paper (F. S. Co. No. 11-995) held taut in a carriage (Fig. V-30) of special design. This method did not fulfill the specifications of the Federation but was practically free from trouble.

The carriage was machined from a solid aluminum block and had a brass plate on the bottom held by 4 screws. It was designed to take the place of the standard 1-cm. cell carrier of the spectrophotometer. The carrier holes are two positions apart on that instrument's positioning rod, which must be adjusted slightly so that the holes in the carriage line up with the exit slit of the spectrophotometer. To ready the carriage for use, two strips of lens paper about 30 × 60 mm. were cut and their lower ends inserted between the brass plate and the aluminum block. The screws were tightened to hold these ends, and the upper ends were drawn taut and secured with Scotch tape.

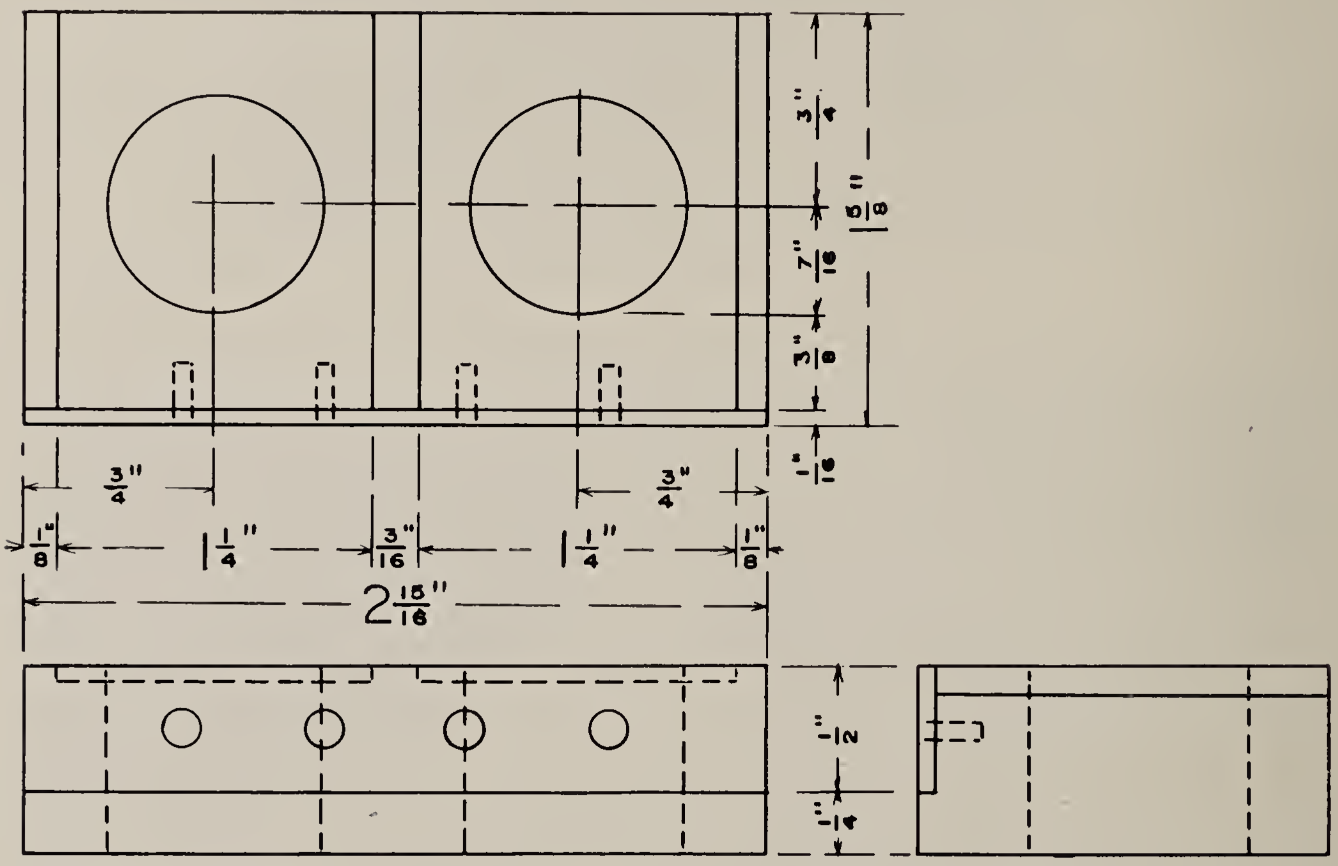


Fig. V-30. Carriage for films cast on lens paper for spectrophotometer scanning.

Two drops of a 1:1 solution of n-butyl stearate in cyclohexane (spectroscopically pure) were placed by means of a hypodermic syringe on the "blank" strip, and spread in a circular motion radiating from the center by the "flat" of the needle. The blank was allowed to remain 72 hours in the drying cabinet; in that period its ultraviolet spectrum became stable. Two drops of a 1:1 solution of the sample in cyclohexane were then applied in the same manner to the other strip. If, after spreading, the sample was found not within the best optical-density range, a drop of cyclohexane was added and the deposit thinned by repeating the spreading motion. Initial readings were made at once.

Samples were dried at average conditions of 26.8° C., 49% relative humidity, and 25 foot-candles of light from a daylight fluorescent lamp. Unfortunately, since the laboratory air-conditioning facilities were out of use at the time, temperature and humidity readings are averages over the entire drying period. The drying cabinet which had been especially built for these experiments could not entirely cope with the large variations of normal summer weather, as it was designed merely to supplement the air conditioner.

The compounds measured were PE and diPE oleates, trilinolein, PE and diPE linoleates, and PE and diPE linolenates. From the ampules, they were transferred to vaccine bottles and sealed with a rubber diaphragm under a slight positive pressure of carbon dioxide gas. Care was taken that they did not come into contact with the rubber.

Measurements

The spectra were determined at about 2-hour intervals up to the set-to-touch time and at gradually lengthening intervals thereafter. Measurements were made at points 2.5 mμ apart, using initially an average nominal band width of 1.0 mμ, which was increased to about 1.4 mμ in the region of 210 to 220 mμ and above 290 mμ to allow sufficient light through the sample. Conventionally, optical absorption is reported by plotting extinction coefficients or absorptivities against wavelength in millimicrons, or wave number in cm.$^{-1}$. However, to use such coefficients the amount of material in the light beam must be known—in this case the thickness of the film, which could not be accurately measured. Therefore the standard plot of optical density against wavelength as recommended by Jones (38) was used.

Oleates

Previous workers (3,33,61) in oxidation of oleates isolated two monohydroperoxides, of which the 11-isomer appeared more stable;

they suggest that union of oxygen with C=C groups forms much of the autoxidation product. Ketols and vicinal dicarbonyl compounds do not accumulate in oxidized monoethenoic acids in more than trace amounts; conjugated, carbonyl-containing unsaturated systems account for increased optical absorption. Others (22) claim that alpha, beta-unsaturated keto acids are initial products of autoxidation and are peroxide-forming.

Ultraviolet absorption does not detect the formation of hydroperoxides, but it is affected by the appearance or disappearance of conjugation. In this connection, it should be remembered that hydroperoxides can undergo intramolecular dehydration to yield carbonyl groups, which can be detected if in conjugation with other double bonds.

The spectra in Fig. V-31 of PE and diPE oleates show that from

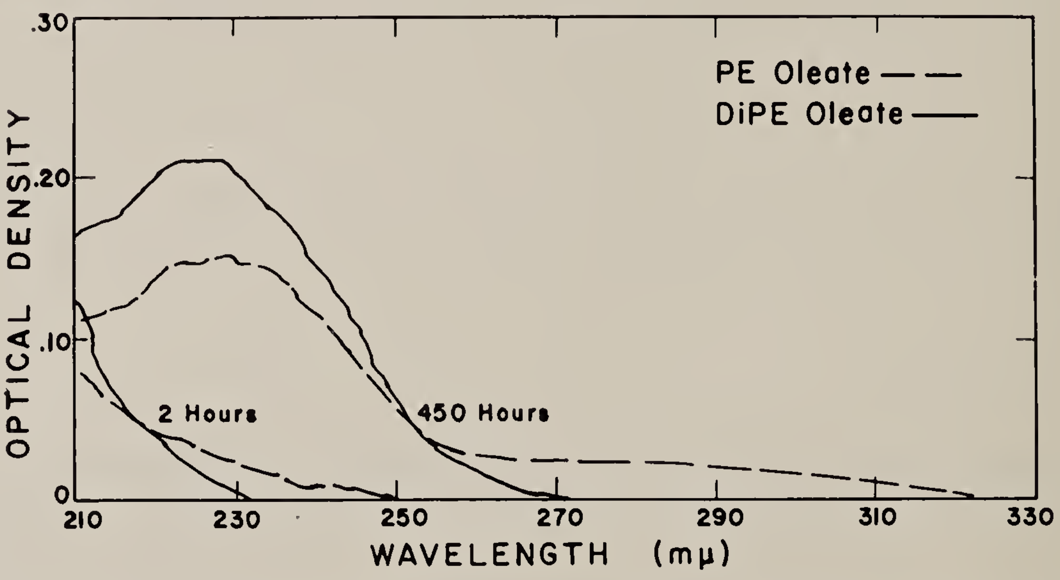


Fig. V-31. Optical densities of UV spectra of PE and diPE oleates.

2 hours age to the set-to-touch time (about 450 hours) there is an increase in the absorption at 232.5 mμ, corresponding to two conjugated double bonds. They are in agreement with those reported by Chevalier and Burg (19) for triolein. On plotting optical density at 215.0 and 232.5 mμ against time, the curves in Fig. V-32 were obtained; they resemble those of Chevalier and Burg (18). Evidently the absorption-time curve for 215.0 mμ approximately parallels that for 232.5 mμ. Since absorption at 215.0 mμ corresponds to the chromophore C=C—C=O (15), this parallelism is easily understood.

H. W. Thompson (64) has stated that the extent of a polymeriza-

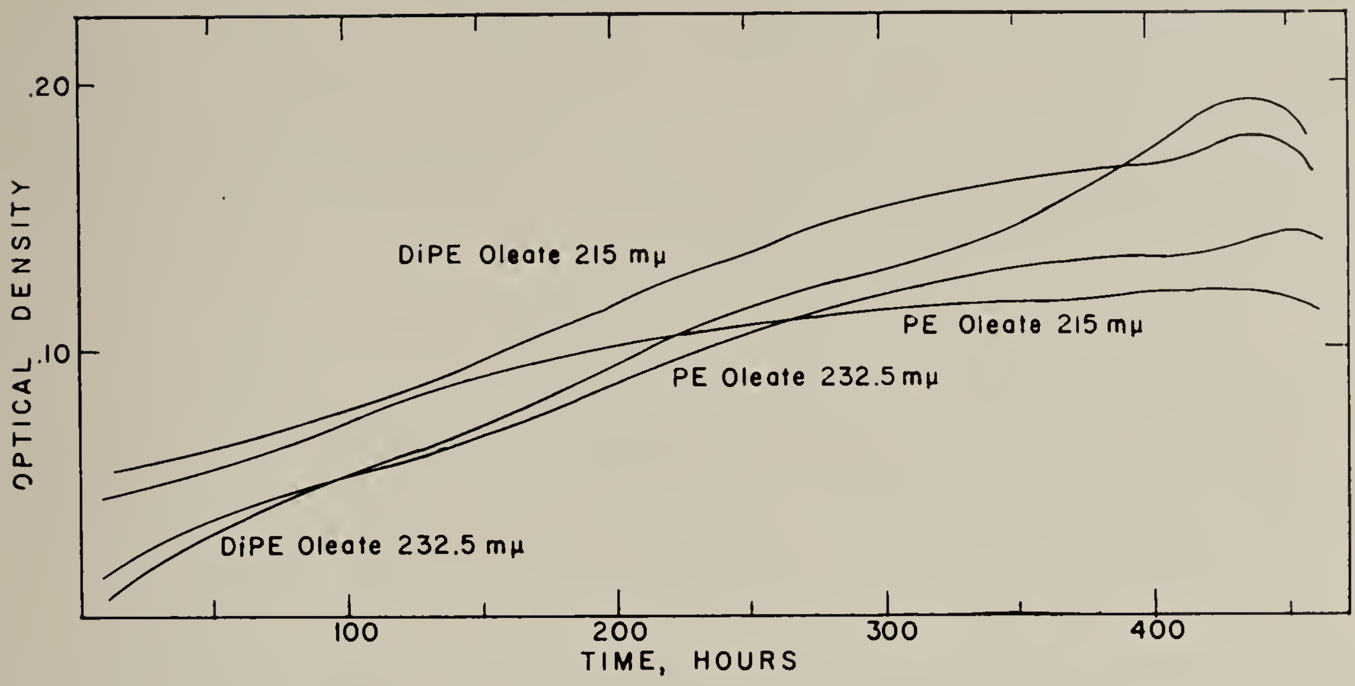


Fig. V-32. PE and diPE oleates: changes in optical density at 215 and 232.5 mμ with time.

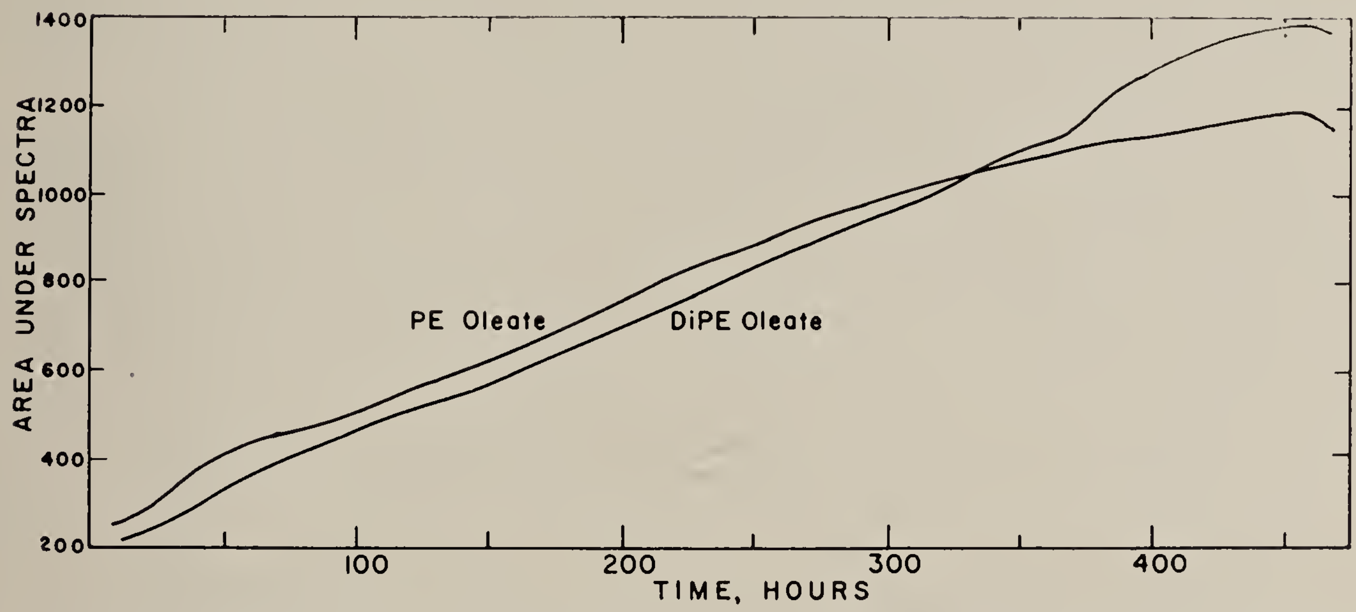


Fig. V-33. Oleate esters: changes in area under UV absorption curves with time.

tion reaction may be measured by the area under an ultraviolet absorption-wavelength curve. Such areas for the two oleates are plotted against time in Fig. V-33.

Linoleates

The presence of the bond system —CH=CH—CH$_2$—CH=CH— causes a marked increase in the ease of oxidation. Though the absorption-time curves may differ considerably, the mechanism of reaction may be the same.

Absorption spectra for trilinolein, PE linoleate, and diPE linoleate are given in Figs. V-34, V-35, and V-36. These curves are selected from many that were prepared; they show the absorption at 2 hours, set-to-touch time, and 625 hours after exposure. The following regions of absorption are significant:

Wavelength (mμ)	Chromophore	Ref.
217.0, 321.0 (weak)	$-C=C-C=O$	15
230.0	2 conjugated double bonds	12
245.0, 285.0, 435.0 (weak)	*p*-Benzoquinone	16
262.0 (weak), 270.0, 282.0	3 conjugated double bonds	12
299.0, 311.0	4 conjugated double bonds	12

All samples absorb strongly in the 230-, 250-, and 270-mμ regions at the set-to-touch time. This absorption gradually falls off and then rises until the general shape of the 625-hour curve is attained. This growth, decay, and regrowth is illustrated in plots of optical density against time (from 0 to 800 hours) for the wavelengths 232.5, 247.5, 270.0, and 300 mμ, in Figs. V-37, V-38, and V-39.

In all cases maxima at 300.0 mμ, corresponding to four double bonds, occurred after those corresponding to two and three conjugated double bonds. Areas under spectra are plotted in Fig. V-40.

Linolenates dry by a mechanism similar to that of linoleates but at a faster rate (9). Spectra of PE and diPE linolenates, at 2 hours,

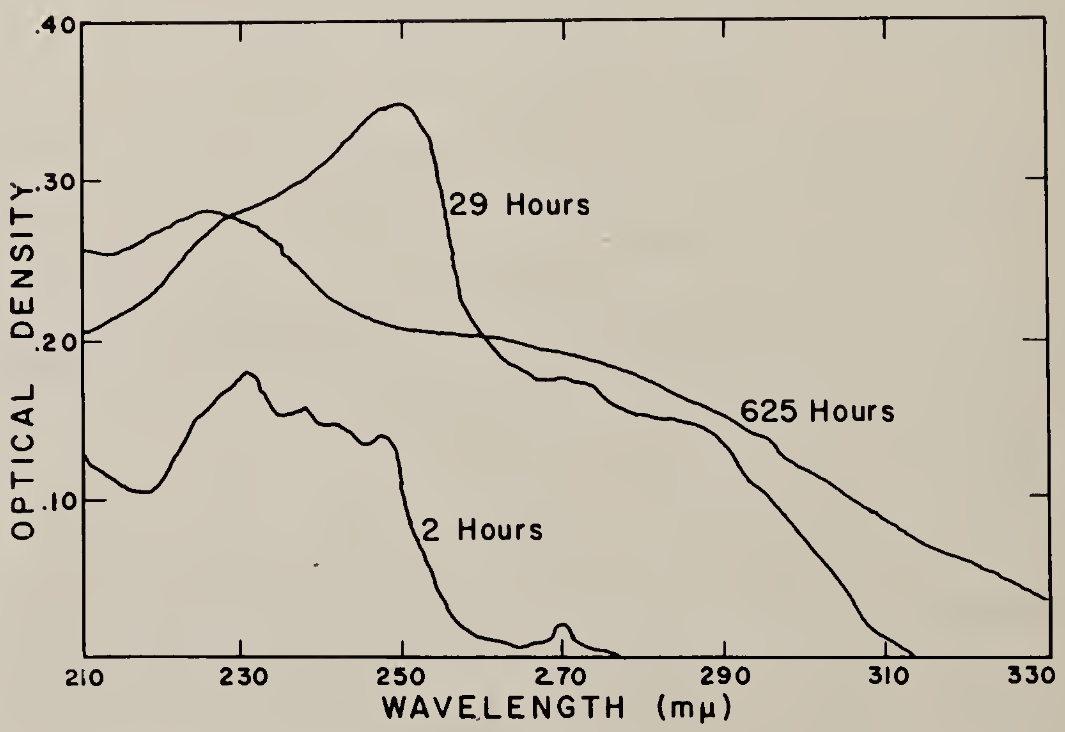


Fig. V-34. Optical densities of UV spectra of trilinolein.

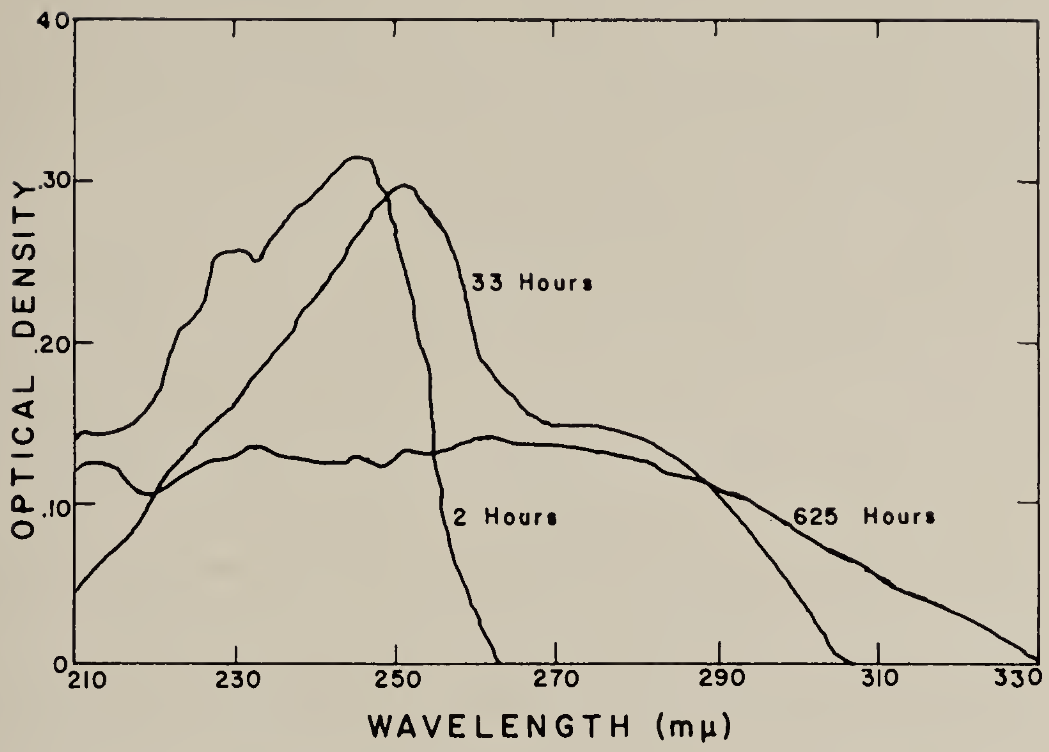


Fig. V-35. Optical densities of UV spectra of PE linoleate.

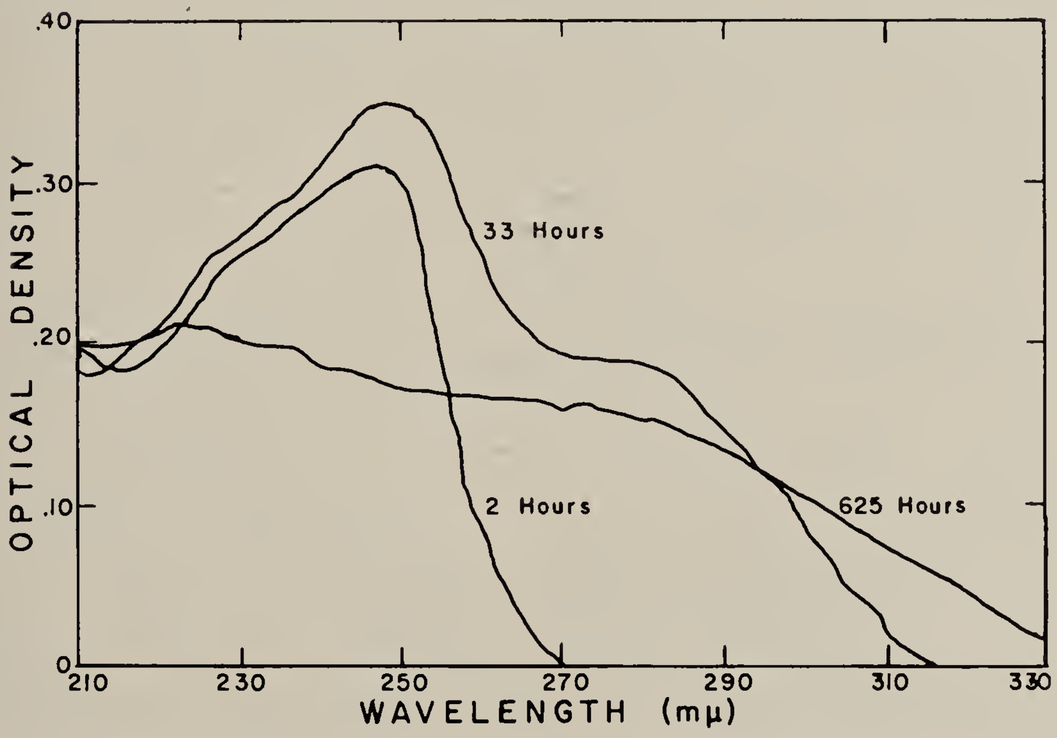


Fig. V-36. Optical densities of UV spectra of diPE linoleate.

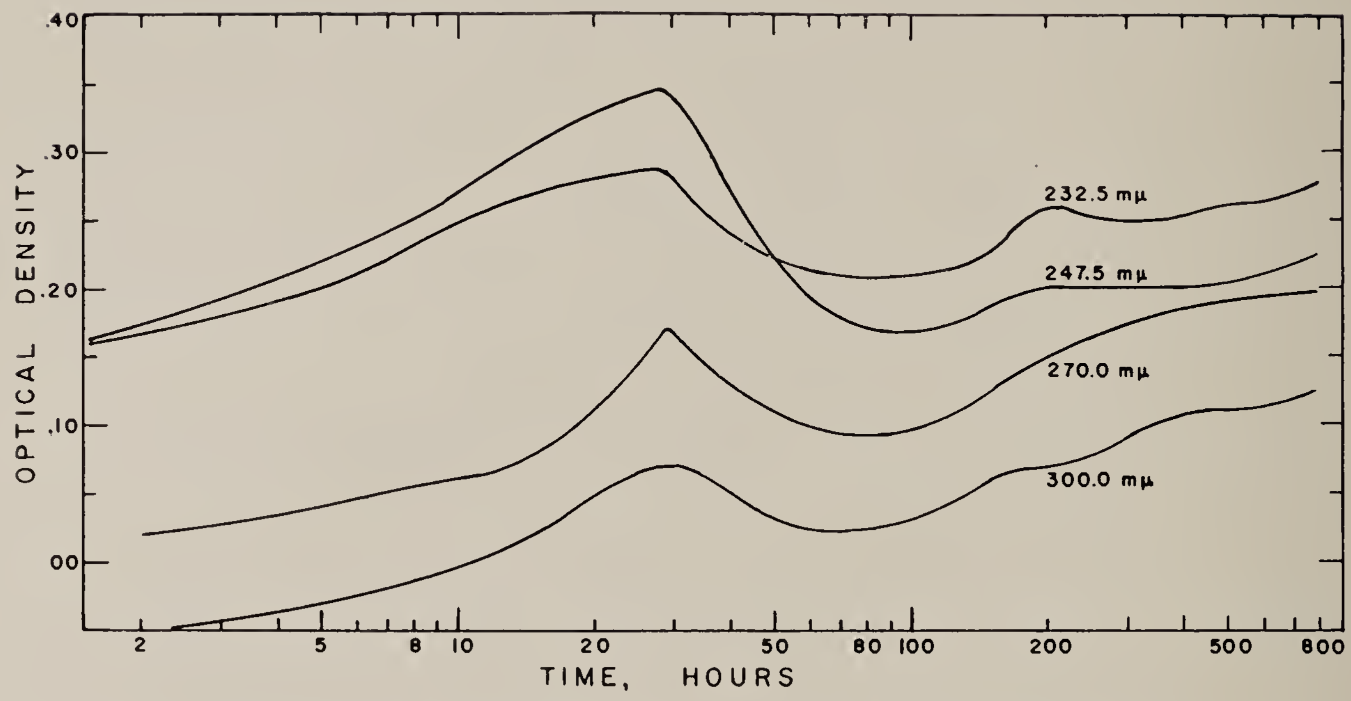


Fig. V-37. Trilinolein: changes in optical density in selected regions with time.

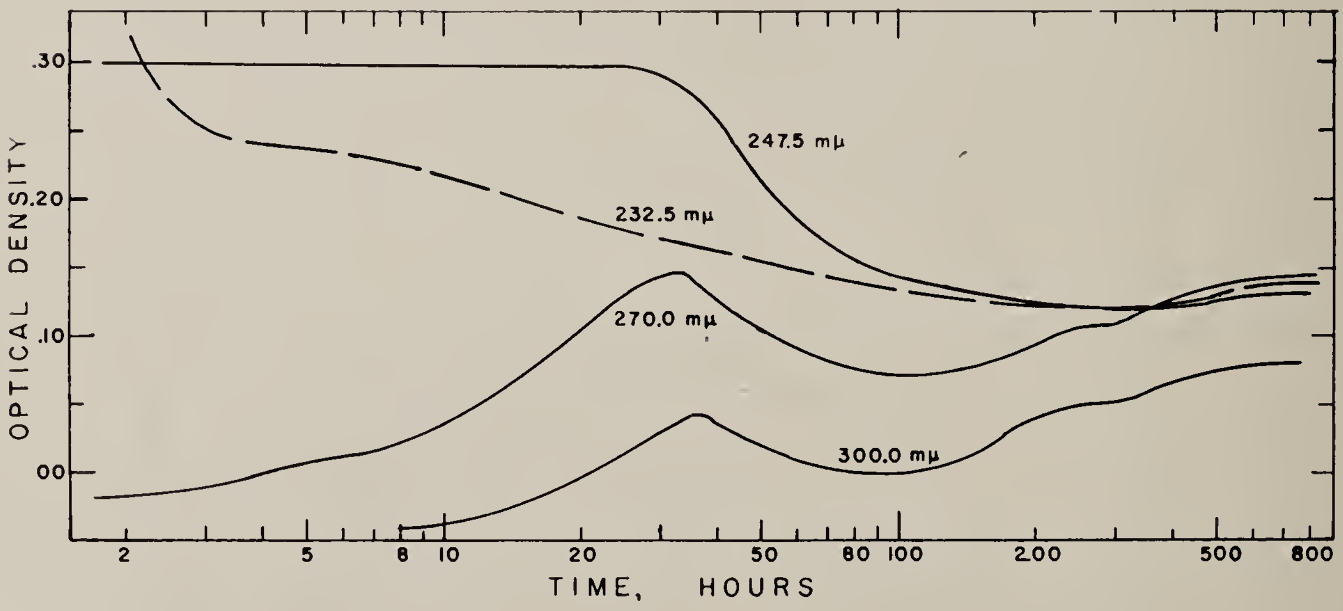


Fig. V-38. PE linoleate: changes in optical density in selected regions with time.

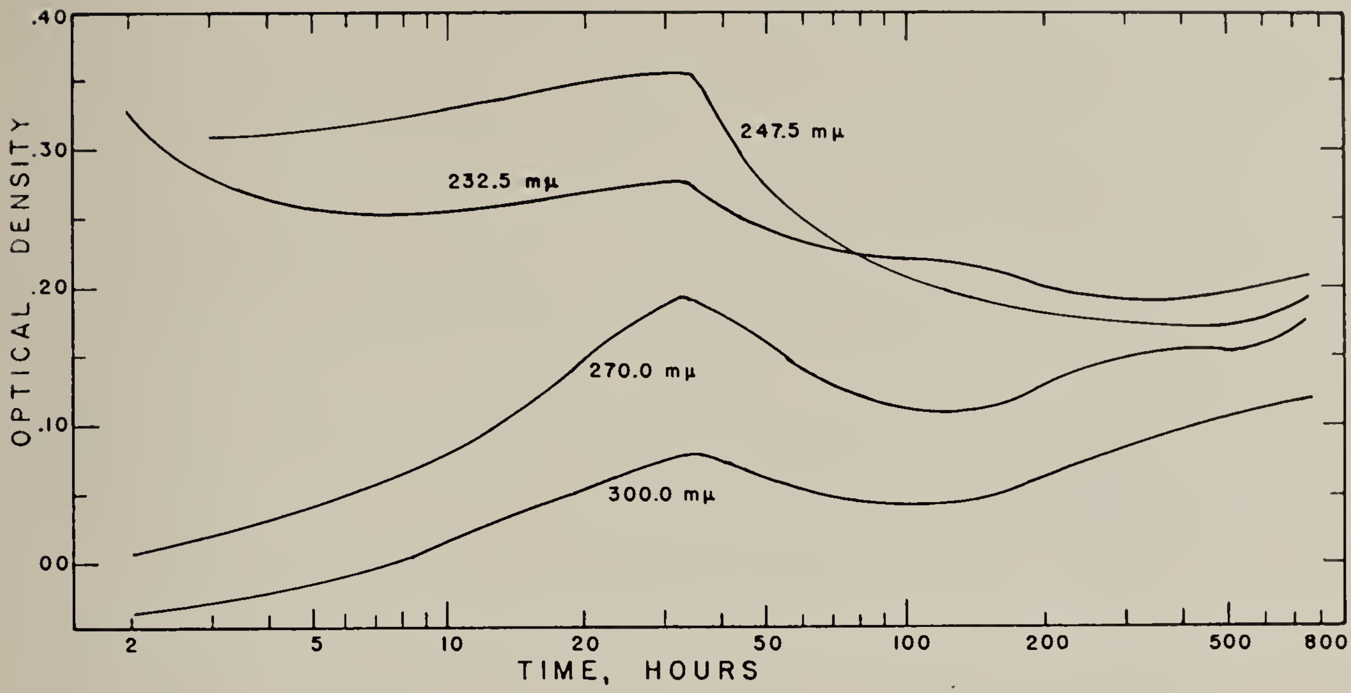


Fig. V-39. DiPE linoleate: changes in optical density in selected regions with time.

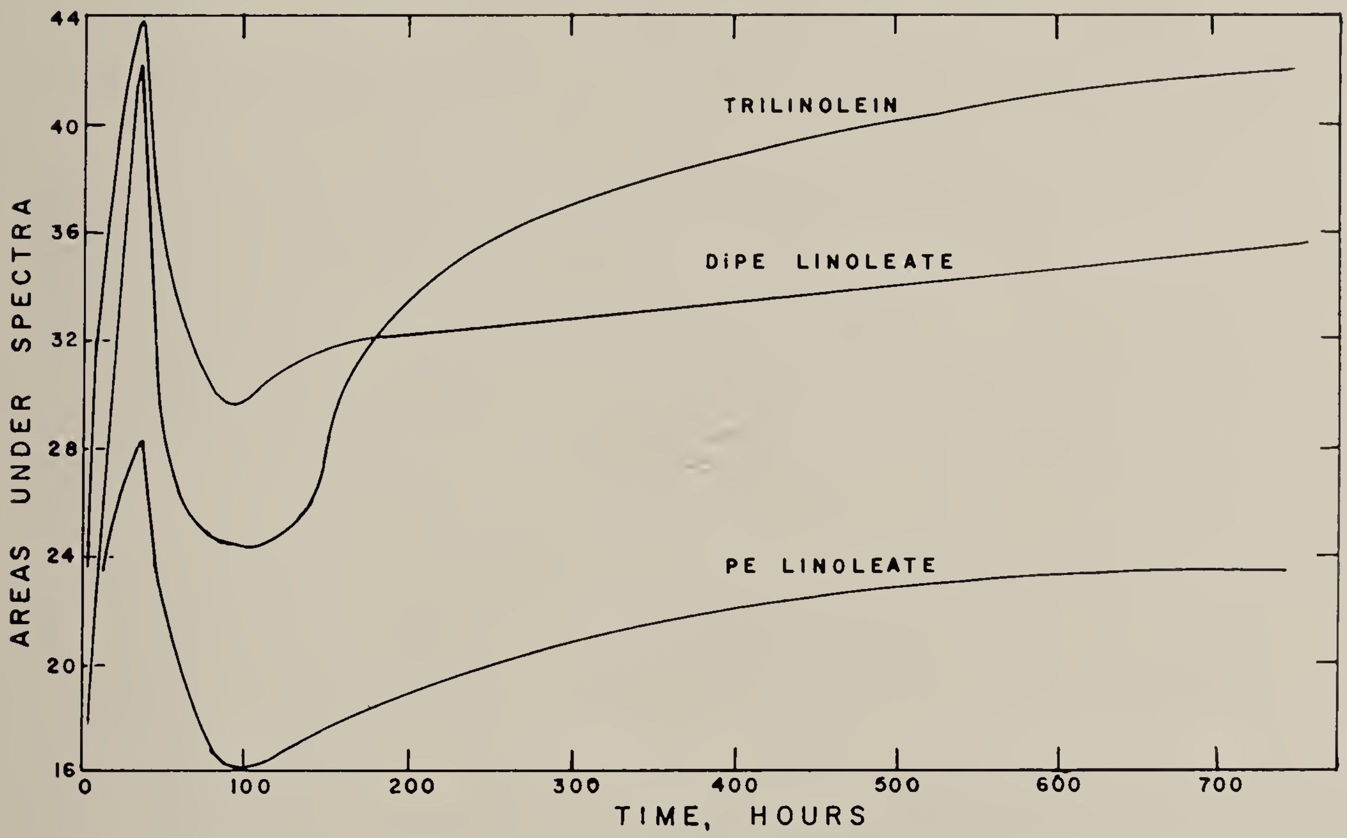


Fig. V-40. Linoleate esters: changes in area under UV absorption curves with time.

set-to-touch time, and 433 hours after exposure appear in Figs. V-41 and V-42; setting times were, respectively, 12 and 10 hours. Significant wavelengths and other general features are the same as for linoleates. Plots against time up to 500 hours are shown in Figs. V-43

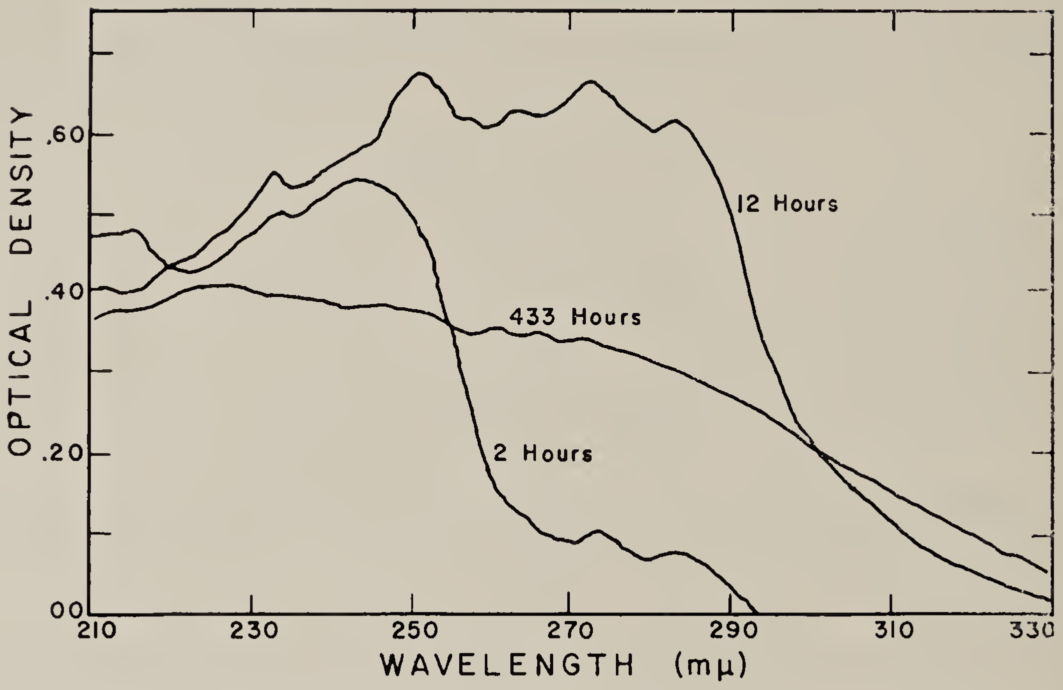


Fig. V-41. Optical densities of UV spectra of PE linolenate.

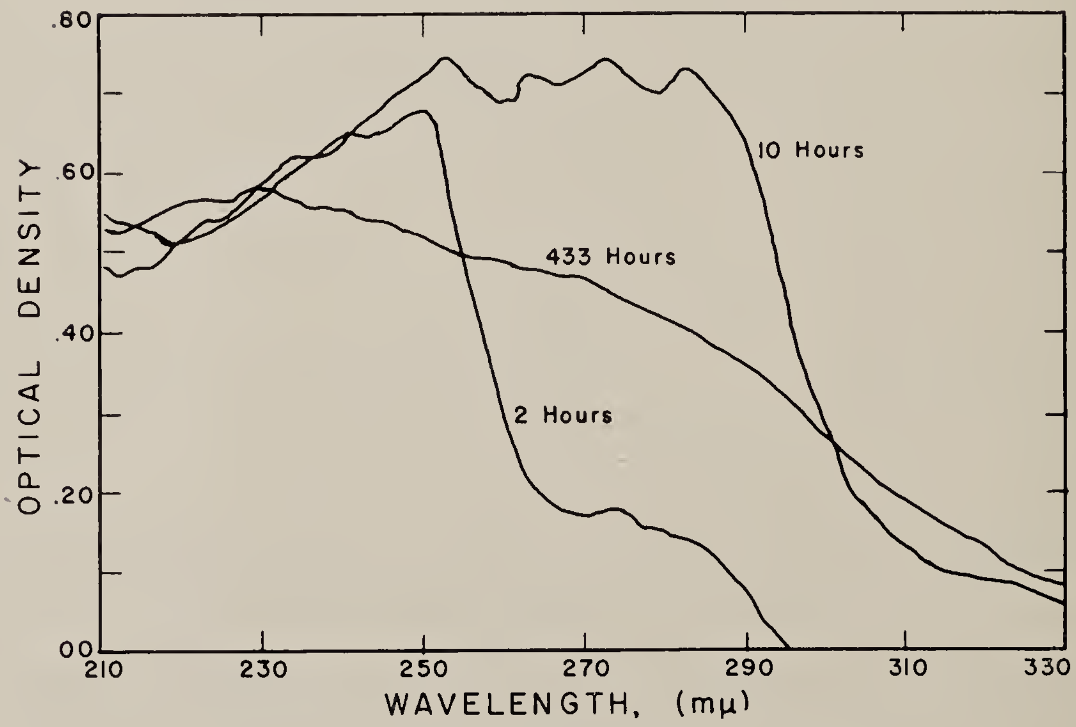


Fig. V-42. Optical densities of UV spectra of diPE linolenate.

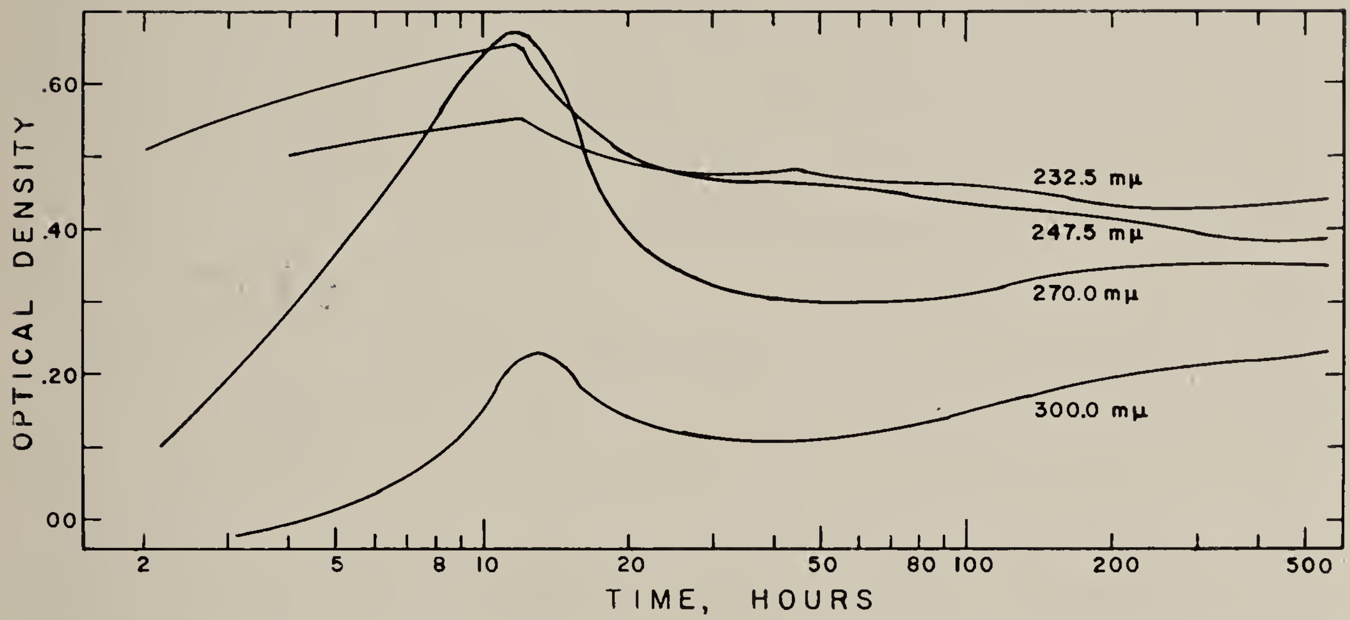


Fig. V-43. PE linolenate: changes in optical density in selected regions with time.

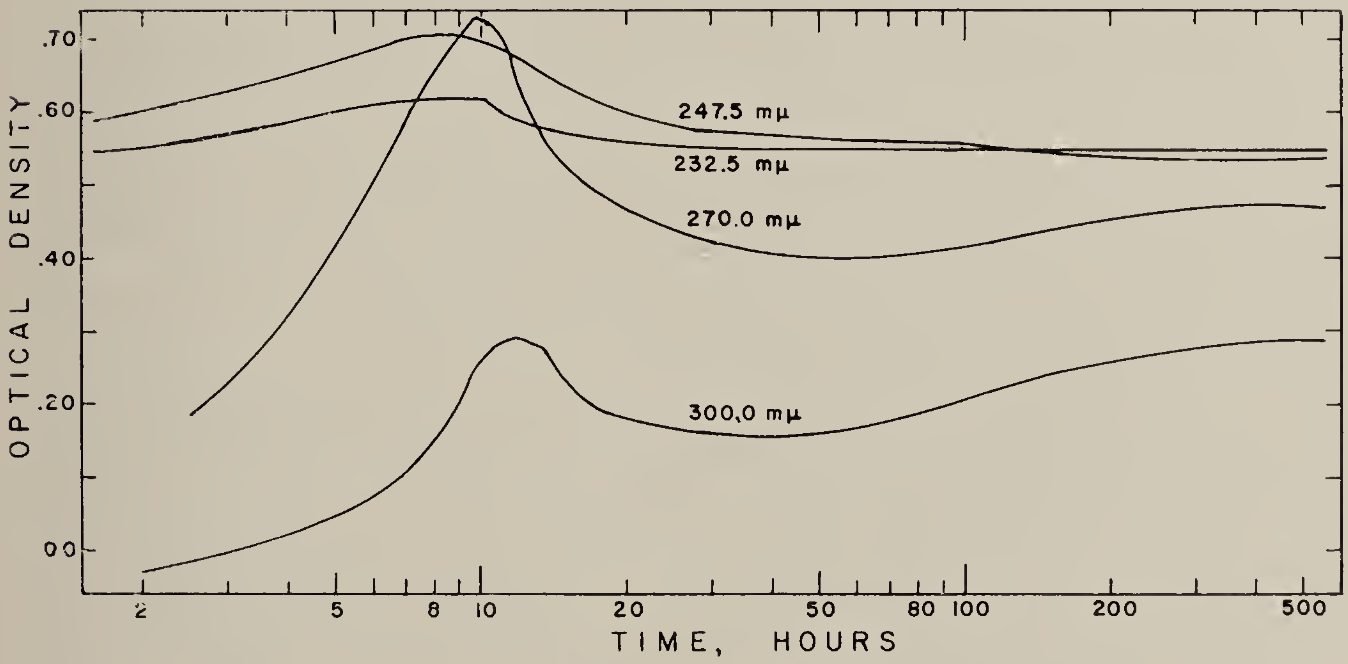


Fig. V-44. DiPE linolenate: changes in optical density in selected regions with time.

and V-44. A curve (Fig. V-45) showing how the area under the spectrum curves varies with time has a shape similar to that of these other curves.

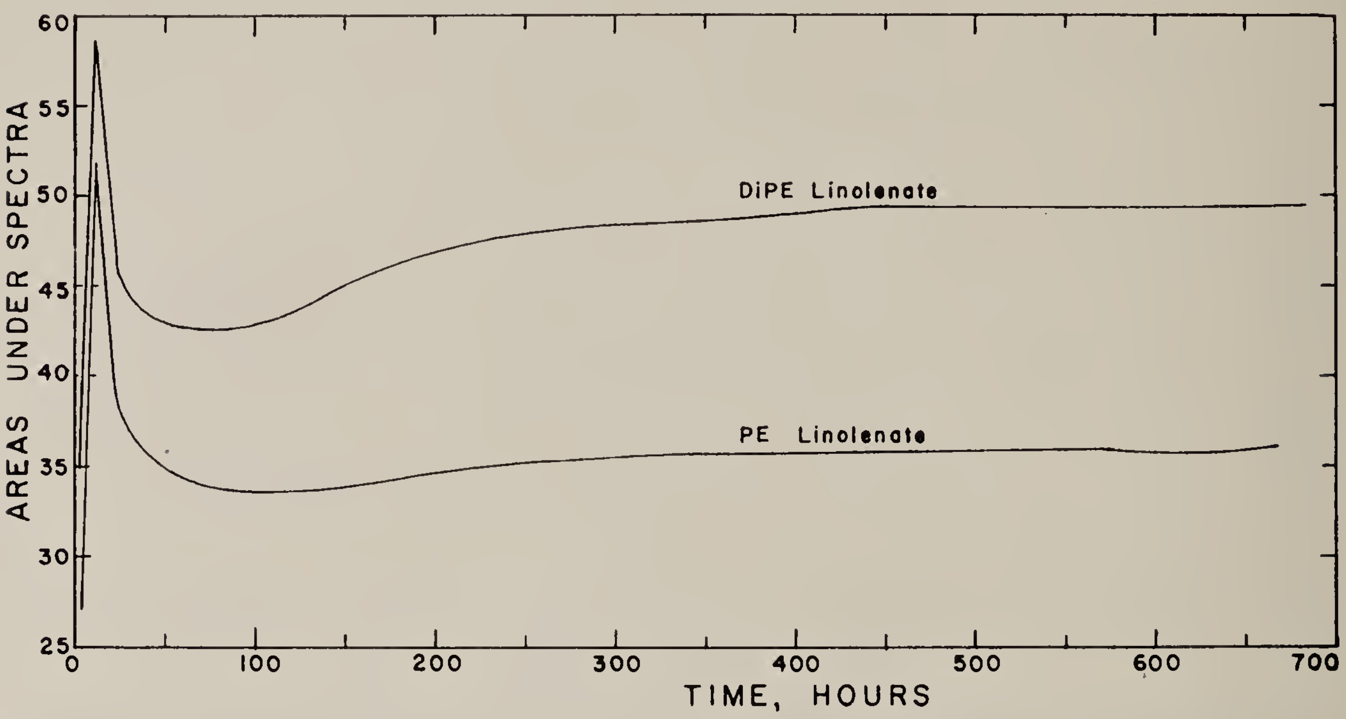


Fig. V-45. Linolenate esters: changes in area under UV absorption curves with time.

Ultraviolet Spectra, Project 24—The Hormel Institute

As in the case of the infrared spectral readings at The Hormel Institute, the ultraviolet readings made there were a part of Project 24, "Oxidation Studies." This was a research which attempted to correlate the rise and fall of peroxide content during drying with other phenomena of the oxidation process.

A radically different procedure was used in obtaining the spectrophotometric data, and instead of reporting complete spectral curves, the Hormel Institute team plotted, against the amount of oxygen absorbed, the UV absorption at certain specific wavelengths characteristic of the various degrees of conjugated unsaturation. The data, although consequently not directly comparable with the results presented in this chapter, parallel very closely the findings of Project 6c. They are given and discussed in detail in Chapter XIII.

Discussion

McAdie and Nicholls proposed a mechanism based on evidence obtained by themselves and others for the initial phases of the autoxidation process for oleates; later phases need more study for their elucidation. A free radical is first formed by loss of an alpha-methylenic hydrogen atom through the agency of light, heat, or oxygen; or a pi-complex, cyclic peroxide, or diradical may be formed by addition of oxygen to the olefinic double bond. These initially formed substances then lead to the formation of unsaturated peroxides (hydroperoxides) with or without migration of the C=C bond. Dehydration to an alpha, beta-unsaturated ketone is stressed as one of the breakdown products of this hydroperoxide, although there are other possibilities, such as free radical, cyclic oxide, and ketol formation (60).

Investigators of the oxidation of methyl linoleate have disagreed about the nature of the products. Lundberg (42) reported monomeric hydroperoxides, mostly conjugated, and a minor amount of diperoxides. He also found (44) that mainly the 9- and 13-hydroperoxides are formed, together with a diperoxide to some extent, possibly by the 1,4 addition of oxygen to the 9- and 13-conjugated hydroperoxides. Bergström (7) found no evidence in proof of a 11-hydroperoxide. Mukherjee (46), using chromatographic separation techniques, obtained results which led him to envision oxidative attack at the alpha-methylene group, resulting in the formation of the 11-hydroperoxide, which then rearranges to 9- and 13-hydroperoxides with conjugated double bonds. Treibs (65) stated that in autoxidation of methyl linoleate 2 moles of oxygen are absorbed and dialkyl peroxides are formed. He suggests that an alpha-methylene group loses a hydrogen atom, allylic rearrangement occurs, and a conjugated system is formed. One molecule of oxygen adds to one double bond to form a peroxide, which stabilizes itself by addition to a double bond of the same or another fatty acid residue; the second molecule saturates the remaining double bond and the resulting peroxide rearranges to an alpha-ketol group.

Bolland and Koch (10) interpret spectroscopic analysis as proving that oxidative attack at the alpha-methylene group results in formation of a free radical, a resonance hybrid of three canonical forms; the free radical is stabilized by addition of oxygen, and a hydrogen radical from another linoleate (35). Two of these forms are conjugated dienes. Absorption at 275 mμ, they think, represents decomposition of the conjugated hydroperoxide to form a conjugated diene ketone. Bateman and Gee (5) also have shown the initial reaction with methyl linoleate to be the photolytic generation of free radicals and the dominant chain initiation process thereafter is photolysis of olefin hydroperoxide.

McAdie and Nicholls tentatively assigned the maximum at 247.5 $m\mu$ to a *p*-benzoquinone structure; they ascribed its displacement from 245.0 $m\mu$ to bathochromic effects, since no other logical alternative presented itself. Unfortunately, the suggestion could not be checked by reference to quinone absorption at other wavelengths; the region at 285.0 $m\mu$ is too close to that at 282.0 (representing three conjugated double bonds), and that at 435.0 $m\mu$ is too weak to be detected.

Discussion and Evaluation of Ultraviolet Absorption Data

Further evaluation of the UV spectrophotometric changes is presented in Chapter XIII. The methods used in Project 6c have the advantage that direct scanning of the same film can be continued over a long period of time after the film has become hard, and the disadvantage that they must be confined to very thin films, within the limitations of the spectrophotometer. The method of Project 24 (taking the readings on fatty acid residues obtained by reduction and hydrolysis of the films prepared on glass plates) has the advantage of much versatility insofar as measurements up to the setting point or slightly beyond are concerned, but is subject to considerable error as the film age increases beyond this point. Obviously the secondary reactions that take place in aging and deteriorating films will alter the spectral absorption, but many such spectral changes will be lost in the method involving reduction and hydrolysis.

The good correspondence between results of the two procedures validates the techniques and indicates that the two methods complement each other usefully. The data confirm and extend the knowledge gained by previous workers in this field. An important contribution of the McGill University project was the development of the technique for direct measurement of changes in spectral absorption in thin films.

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CHAPTER VI

Outdoor Exposure Tests

Since "Film Deterioration" was a major division of the research program, a study of the effects of natural and artificial weathering conditions on the pure compounds, both clear and pigmented, was of course important. Three of the projects involved such a study. In two of them, which will be discussed in Chapter VII, exposures were made in a Weather-Ometer, and various chemical and physical measurements were made to follow the progress of deterioration. In Project 8, outdoor exposures were made and careful records were kept, as in the customary supervision of test fences in the paint industry, of visual evidences of decay.

Outdoor Exposure Tests, Project 8—C.D.I.C. Club

This project was taken in hand by the Columbus Technical Committee of the C.D.I.C. Club (L. P. Larson, Chairman; Benson Brand, Kenneth Jackson, William Kentner, E. E. McSweeney, Chester Olson), the same group which, with added personnel, successfully carried out the important work of preparing pigmented coatings from the Federation vehicles. A report of the first seven months results appeared in the *Official Digest,* No. 311, 1033 (December, 1950). The final report, with editorial changes, is presented here.

Preparatory Work

Materials used in the exposure tests included all the Federation compounds in both clear and pigmented form, except No. 19, SO eleostearic glycerol alkyd, which gelled before it could be applied, and the clear PE and diPE oleates, which did not dry. As controls, in addition to the pigmented commercial vehicles Nos. 1, 2, and 3, two commercial outside white house paints and one commercial enamel were also exposed. Both of these house paints contained zinc oxide, titanium dioxide, and magnesium silicate; one also contained lead pigment. The vehicles of both were conventional blends of raw and bodied linseed oils, with thinner and drier. The enamel contained titanium dioxide in a commercial alkyd vehicle.

The Federation drier was added in prescribed proportions to both the clear and the pigmented pure compounds; the tubes were resealed under nitrogen, and the contents were mixed by vigorous shaking. Pigmented compounds Nos. 1 to 8 were held 48 hours before being drawn down for exposure; the other pigmented compounds and the clear compounds were held 72 hours.

All exposures were made in duplicate on polished plate glass panels 9 × 12 inches in size. The panels were cleaned with pumice, rinsed with distilled water and with absolute alcohol, and swabbed with a 5% alcoholic solution of benzoic acid, and the excess benzoic acid (after evaporation of the alcohol) was wiped off with a clean rag moistened with alcohol.

When the tubes were again opened, the paints were thoroughly stirred with a spatula, their condition noted, and the fineness of grind determined on the Hegman Fineness Gauge. The small amounts of vehicle available had limited the mill processing to one pass; consequently the fineness was found to range within the limits customary for house paints rather than for enamels, i.e., three to six, with most samples at four or five.

Consistency varied greatly. All the alkyd paints and that made from dehydrated castor oil were long and stringy, like enamels; the others were short and puffy like linseed house paints. The paints made from simple esters took from 10 to 19% of added solvent to bring them to medium consistency. Of those made from alkyds, the LO eleostearic glycerol paint was thick, the SO linoleic glycol and SO oleic PE medium in body, the others thin; the three containing long-oil pentaerythritol alkyds were all as thin as water. The paints made from the control vehicles were brought to medium consistency, No. 1 with 1%, No. 2 (DHC) with 14%, No. 3 (commercial alkyd) with 27% mineral spirits. The group working on this project was the only one that reported relative consistencies in detail.

Application of the samples to the glass plates was by means of a 6-inch adjustable Baker cylindrical drawdown blade. The wet film thickness required for each paint to produce a dry film thickness of

2.5 mils was first calculated, and the blade set for this thickness. A puddle of paint was placed on the panel, and the operator pulled the blade with extended arm and a steady slow movement across the puddle (Fig. VI-1). With an Interchemical Wet Film Gauge, the thickness of film was immediately determined at opposite ends of the panel. If the reading did not correspond with the calculated figure, the Baker blade was reset for the duplicate drawdown on the other panel. A similar procedure was followed in laying films of approximately 1.25 mils dry thickness with the clears.

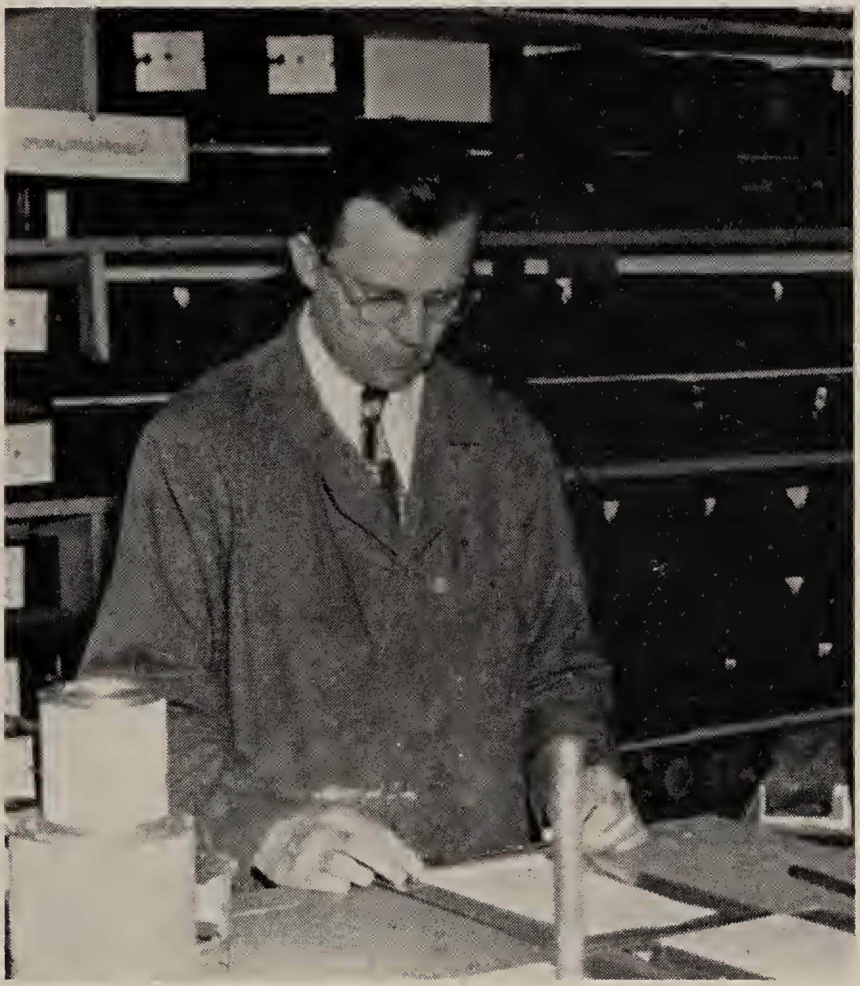

Fig. VI-1. Applying a pigmented sample by means of 6-inch Baker blade.

The paint made from No. 1, linseed oil, was so "short" that it left a ribbed or "corduroy" film; that from PE eleostearate was also ribbed, but partly owing to skins. Specks, either of lint or minute gelled particles, were noted in several alkyd paints; LO linolenic glycerol, LO eleostearic glycerol, LO linoleic PE, LO linolenic PE, and SO oleic PE appeared to have the most.

Crawling was encountered in several of the clears, but pigmentation in most cases overcame that tendency. The clear PE and diPE oleates and diPE linoleate crawled badly. The eleostearate esters crawled and frosted, and the three linolenic esters crawled slightly. Of the alkyds, the LO oleic PE crawled a little, as did the film on one panel of SO linolenic glycerol. The other panels showed fairly smooth, continuous films. A few drops of zinc naphthenate were added to the LO eleostearic glycerol alkyd to minimize wrinkling. In contrast, the PE and diPE oleate paints laid smooth films, but that made from LO oleic PE alkyd crawled badly. One panel of the PE linolenate paint was smooth; the other crawled. Both the linoleic and linolenic short-oil glycerol alkyd paints appeared smooth and continuous when viewed by reflected light, but transmitted light showed thin spots.

The films were applied in the Battelle Institute's constant-temperature (78° F.), constant-humidity (50%) room, and the panels were racked in the same room horizontally under 25 foot-candle illumination for 24 hours, then vertically (unless still too wet) until exposed. Most of the paints dried overnight, but those made from PE and diPE oleates could not be put out for 7 weeks. Three of the glycerol alkyd paints—SO linoleic, LO linolenic, and LO eleostearic—set to touch in 20, 60, and 45 minutes, respectively; but those made from dehydrated castor oil, trilinolein, trieleostearin, and LO oleic PE alkyd, as well as the leaded commercial paint, were tacky at the end of the week.

The clear films were appreciably slower in drying, as shown by Table VI-1. Those of varnish linseed oil and dehydrated castor oil, trilinolein, and PE linoleate were still tacky when exposed, 10 days after application, and remained so (the linseed oil even appearing to become wetter for some months) for 27 weeks. Trieleostearin and LO oleic glycerol alkyd took about 13 weeks to dry.

The edges of all the films were protected from moisture seepage by applying an aluminum paint made from Reynolds Metals Co.'s No. 20 Paste in American Cyanamid Co.'s Rezyl No. 869-1; this was also spotted on the places where the Interchemical thickness gauge measurements had been made.

All the paints were exposed on March 24, 1950, except the two oleates, which went out on May 12. The clears, drawn down on March 23, were exposed on April 3. The panels were mounted vertically, facing south, on the American Zinc Sales Company test

TABLE VI-1

Film Characteristics of Clear and Pigmented Compounds for Exterior Exposure Tests

	Clear				Pigmented					
		Wet film thickness (mils)						Wet film thickness (mils)		
						Solids (%)				
Compound	Solids (%)	Required	Setting	Obtained	Fineness	Tot.	Veh.	Required	Setting	Obtained
Trilinolein	100	1.25	1.50	1.4–1.8	4–5	73.4	51.4	2.43	2.4	3.0
			1.50	1.4–1.6					2.0	2.0–2.4
Trilinolenin	100	1.25	1.50	1.4–2.0	4	77.9	54.6	2.29	2.0	2.6
				1.0–2.0					2.0	2.6–3.0
Trieleostearin	100	1.25	1.25	1.8–1.9	4–5	68.9	48.2	2.60	4.5	4.0
			1.00	1.2–1.4					3.5	3.8
PE oleate	100	1.25	1.25	1.8–1.9	4–5	67.0	46.9	2.67	2.4	1.9–2.6
			1.00	1.2–1.4					2.4	2.0–2.4
PE linoleate	100	1.25	1.50	1.5–1.8	3	65.3	45.7	2.74	2.8	3.6
			1.25	1.0–1.6					2.5	2.6
PE linolenate	100	1.25	1.25	1.6–2.0	4–5	67.8	47.4	2.64	3.0	2.8
									2.7	2.4–2.7
PE eleostearate	100	1.25	1.00	1.0–1.1	4–5	66.2	46.3	2.70	3.5	3.0–3.4
			1.25	1.0–1.4					3.0	3.0
DiPE oleate	100	1.25	1.25		5	62.5	43.7	2.86	3.5	3.0
									3.5	3.0–3.1
DiPE linoleate	100	1.25	1.25		5	62.9	44.0	2.84	3.5	3.0–3.2
									3.0	3.2
DiPE linolenate	100	1.25	1.25	1.0–1.4	4–5	72.0	50.4	2.47	3.0	2.4
				1.4					3.0	3.1
LO linoleic glyc. alkyd	50	2.50	2.50	2.0–2.2	4	50.4	35.3	3.54	6.0	4–
				2.0–2.4					5.0	4–
LO linolenic glyc. alkyd	50	2.50	2.50	2.8	4–5	50.4	35.3	3.53	4.0	3.0–4.0
				2.0–2.6					4.0	3.4
LO eleostearic glyc. alkyd	50	2.50	2.50	2.6	4–5	49.3	34.5	3.62	5.0	3.8
				1.8–2.3					5.0	3.7
SO linoleic glyc. alkyd	50	2.50	2.50	2.8–3.0	4–5	49.3	34.5	3.62	4.0	3.2
			2.25	1.8					4.5	3.4–3.5
SO linolenic glyc. alkyd	50	2.50	2.50	2.4	4–5	49.3	34.5	3.62	4.5	3.4
				2.2–2.6					4.5	3.2–3.8
LO oleic PE alkyd	50	2.50	2.50	2.0–2.4	4–5	50.4	35.2	3.56	3.5	3.2
				1.8–2.7					4.0	3.2–3.6
LO linoleic PE alkyd	50	2.50	2.25	2.0–2.3	4–5	50.4	35.2	3.55	4.0	3.2–3.6
			2.50	2.3–2.4					4.0	3.2–3.8
LO linolenic PE alkyd	50	2.50	2.50	2.4–2.8	4–5	50.4	35.2	3.56	4.0	3.2–3.7
				2.6–3.2					4.0	3.2–3.7
SO oleic PE alkyd	50	2.50	2.50	2.6	3–4	49.3	34.5	3.61	4.5	3.4
				1.8					5.0	3.8
Varnish linseed oil	100	1.25	1.50	1.2–1.7	4–5	97.4	68.2	1.83	1.83	1.80
									3.0	3.0
Dehydrated castor oil	100	1.25	1.50	1.2–1.4	5	70.7	49.5	2.56	2.5	2.4
				2.0–2.5					2.2	2.2
Commercial alkyd	50	2.50	3.00	2.9–3.0	5–6	49.2	34.4	3.63	3.6	2.0
			2.50	1.8–2.0					5.5	3.7
									6.2	4+

fences in a semi-suburban area northeast of Columbus, Ohio (Fig. VI-2).

The gloss of the paint films was read on the day of exposure by means of a Gardner 60° Glossmeter. Readings, on a "per mil" basis, ranged from 15 to 108, with LO linolenic PE alkyd highest, trilinolein lowest, as shown in the first column of Table VI-2.

The clear liquids had a total exposure time only 10 days less than that of the paints, and results are thus comparable. Best of the series at the end was LO linoleic PE alkyd; its films, though specky and with a few holes, were tough and in good condition. They were separating slightly, but not peeling, from the glass. Next was LO oleic PE alkyd, with more holes and some crawling and shrinking. One film of the commercial alkyd wrinkled badly; the other was in fair condition but with considerable separation from the glass. All others had practically disappeared, except the following which, though in poor condition, still had some film remaining: dehydrated castor oil, trilinolenin, PE eleostearate, and diPE and PE linolenates. As between the duplicate films which varied slightly in wet film thickness, the thinner ones peeled sooner than the thicker, for any given compound. Details appear in Table VI-3.

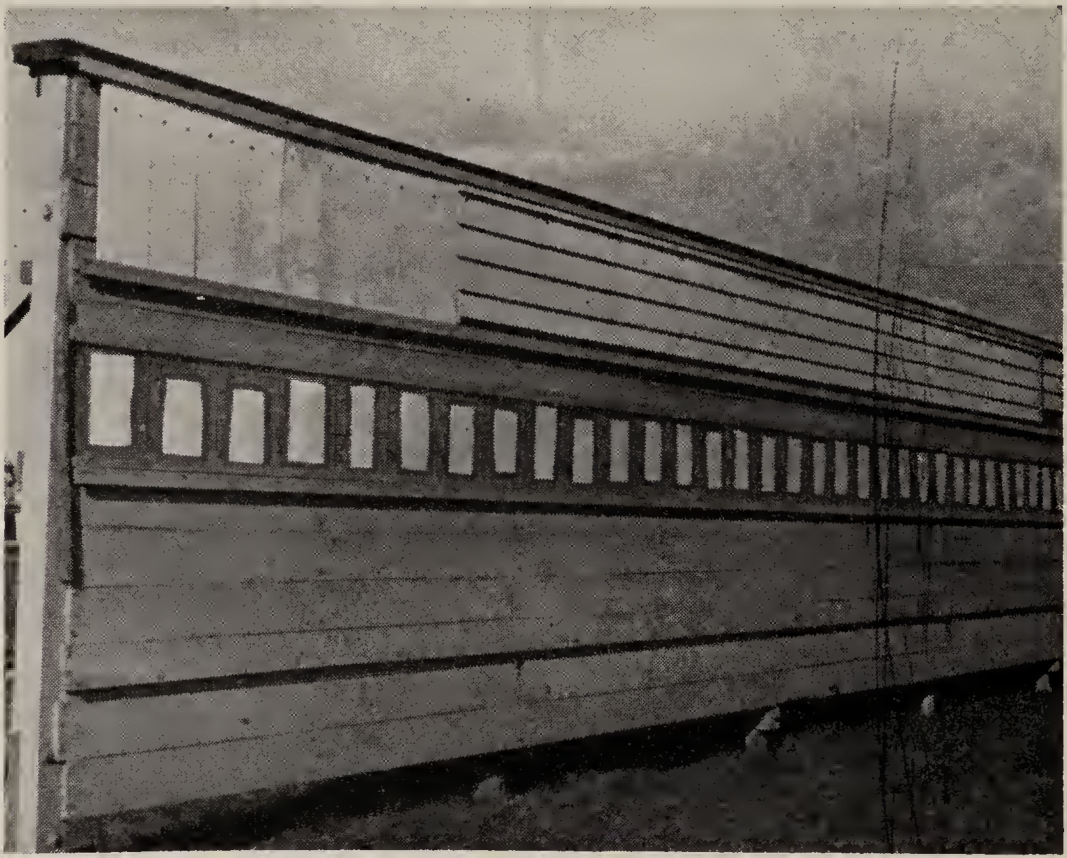

Fig. VI-2. Test fence on which outdoor exposure tests were made.

TABLE VI-2

Changes in Gloss of Pigmented Films on Exterior Exposure (Gardner 60° Glossmeter)

	Weeks of exposure													
Compound	0	2	4	5	6	7	9	10	12	13	14	15	16	24
Trilinolein	15	15	12	11	10	10	10	10	12	10	9	10	8	8
Trilinolenin	70	40	24	13	10	9	10	9	11	10	8	9	7	7
Trieleostearin	71	45	35	25	22	13	10	9	11	9	8	9	7	7
PE oleate	21	21		18	14	12	11						11*	
PE linoleate	35	12	14	10	9	9	10	9	11	10	7	8	7	7
PE linolenate	45	32	25	13	10	9	8	8	12	10	10	10	8	8
PE eleostearate	66	56	55	40	27	17	9	10	12	10	9	10	8	8
DiPE oleate	20	20		15	14	10	9						9*	
DiPE linoleate	25	14	12	10	9	8	8	8	10	10	7	8	7	7
DiPE linolenate	51	36	25	13	11	10	8	9	10	10	8	10	7	7
LO linoleic glycerol alkyd	100	90	82	81	75	75	70	69	55	46	30	18	11	8
LO linolenic glycerol alkyd	90	83	68	78	70	55	22	14	12	9	10	10	8	8
LO eleostearic glycerol alkyd	65	56	48	53	52	50	39	34	16	10	9	9	8	8
SO linoleic glycerol alkyd	94	82	70	62	41	28	14	12	13	10	9	10	8	8
SO linolenic glycerol alkyd	99	88	70	74	59	40	16	13	13	10	9	10	8	8
LO oleic PE alkyd	78	78	53	31	24	15	12	10	11	7	7	8	6	6
LO linoleic PE alkyd	74	64	54	53	52	50	30	21	12	9	8	8	7	7
LO linolenic PE alkyd	108	91	78	71	62	41	16	11	11	8	9	9	8	
SO oleic PE alkyd	40	44	35	25	16	13	11	9	11	9	8	8	8	8
Varnish linseed oil	41	28	23	17	15	14	14	13	14	14	11	12	11	10
Dehydrated castor oil	90	85	74	70	57	50	34	17	14	11	9	10	8	8
Commercial alkyd	80	75	57	40	25	18	12	10	12	10	8	10	8	8
Leaded outside white paint	85	55	49	39	33	20	12	11	10	10	8	8	7	7
Lead-free outside white paint	75	60	52	43	40	29	18	15	11	8	8	8	7	7
Commercial enamel	100	89	86	86	87	83	79	78	75	75	71	72	70	57

* Reading at 17 weeks.

Panels were carefully examined almost every week for 5 or 6 months, then at longer intervals, until they were removed from the fence on November 24, 1951 (20 months for the paints). Weekly observations were necessary in the early stages to follow quick changes in gloss and other properties of the unknown films.

Exposure Results

Readings of 60° specular gloss of the paints continued for 24 weeks, at which point all except the commercial enamel were flat (gloss 11 per mil or less). Actually this state had been reached by the 16th week; and even at the 12th week, only the commercial enamel (with a reading of 75) and LO linoleic glycerol alkyd paint (55) had a gloss as high as 16. At 6 weeks, only seven paints besides the commercial enamel gave a reading over 40. The much better retention of luster by the enamel is explained by the fact that its

TABLE VI-3

Deterioration of Clear Vehicle Films on Exterior Exposure

Compound	Weeks of exposure				Months			
	4	10	13	27	9.5	12.5	15.5	19.5
Trilinolein	v tacky		st, dirty	dry, v dirty		sp	90% bare	90% bare, wr
Trilinolenin	dry		rough	fr, sepg	med sepn	fr, sepn	fr, $^{1}/_{3}$ pld	35–50% bare, plg, flkg
Trieleostearin	fr, v sl tacky		dry, wr, cryst	wr, med dirty		fr	1 p bare, 1 v dirty, thin	2 p alm bare, v sl rough
PE linoleate	sl tacky		sl tacky	dry, rough, v dirty		v dirty, rough	70% bare, sp	99% bare
PE linolenate	dry, sl crlg			sp		sp, fr	fr, 50% bare	35–40% bare, fr, sl plg
PE eleostearate	dry, wr		wr, cryst	cryst		fr	fine wr, bare spots	fr, 25–30% bare
DiPE linoleate	dry	Droplets fr. but adhered throughout exposure						
DiPE linolenate	dry, sl crlg			sp, fr		sp, fr	fr, 40% bare	fr, 35 & 60% bare, flkg
LO linoleic glyc. alkyd	dry			start bls	sl plg	75% bare, plg	fr, 1 bare, 1 65%	fr, 1 bare, 1 70% bare, plg
LO linolenic glyc. alkyd	dry	1 p sepg, poor ad	sepn. in ret pattern	excessive sepn	entirely bare			

LO eleostearic glyc. alkyd	dry			sl sepn, blg	entirely bare			
SO linoleic glyc. alkyd	dry			bad sepn, blg, fine pattern	1 p bare, 1 v bad sepn	entirely bare		
SO linolenic glyc. alkyd	dry, sl crlg	start sepn, ret pattern	bad sepn in spots	bad bls	entirely bare			
LO oleic PE alkyd	sl tacky, crlg		dry, sp	dry, sp		sp, fr	fr, 10% bare	fr, sl shrg, sl blg
LO linoleic PE alkyd	dry					fr, sp	fr	fr, start shrg & blg, specks
LO linolenic PE alkyd	dry			sl blg	entirely bare			
SO oleic PE alkyd	dry		1 p bad sepn	1 p bad sepn	entirely bare			
Varnish linseed oil	v tacky, wr	wet, st	st, v dirty	dry, v v dirty	partly bare	entirely bare		
Dehydrated castor oil	tacky	sl tacky	tacky	dry, wr, rough, dirty		v v dirty, rough	v v dirty, fr	1 p 20% bare, 1 80%; rough, fr
Commercial alkyd	dry						start plg	fr, blg, plg

Key: ad, adhesion; alm, almost; bl (blg), blister (blistering); crlg, crawling; cryst, crystalline; flkg, flaking; fr, frosty; med, medium; p, panel; pld (plg), peeled (peeling); ret, reticulate; sepg (sepn), separating (separation); shrg, shrinking; sl, slight, slightly; sp., spotty; st, sticky; v, very; wr, wrinkled.

pigment volume concentration was much lower than that (30%) of the Federation vehicle paints; its dirt retention was also correspondingly greater, and chalking much less.

Chalking (Table VI-4) was not evident on any of the panels until after about 5 weeks, when seven of the films started to chalk. At 7 weeks chalking was very bad on trilinolenin, bad on trilinolein, diPE linoleate and linolenate, PE linolenate, and SO oleic PE alkyd.

TABLE VI-4

Chalking of Pigmented Films on Exterior Exposure

Ratings are on a scale from 1 (excessive chalking) to 10 (none). Total exposure period for PE and diPE oleates was 7 weeks less than 20 months.

	Weeks of exposure											Months		
Compound	1	2	3	4	5	6	7	9	10	12	15	16	18	20
Trilinolein	10	10	10	9+	8−	6	4	1	1	1	1	1	1	1
Trilinolenin	10	10	10	10	8	6	2	1	1	1	1	1	1	—
Trieleostearin	10	10	10	10	10	10	8	2	2	1	1	1	1	1
PE oleate	10	10	10		10		2*	2		2†				(1)
PE linoleate	10	10	10	10	8	8	6	2	2	1	1‡	1‡	1	1
PE linolenate	10	10	10	10	8	8	4	1	1	1	1	1	1	—
PE eleostearate	10	10	10	10	10	10	10	1	1	1	1	1	1	1
DiPE oleate	10	10	10		10		2*	2		2†				(1)
DiPE linoleate	10	10	10	10	8	8	4	1	1	1	1‡	1‡	1	1
DiPE linolenate	10	10	10	10	8	6	4	1	1	1	1	1	1	—
LO linoleic glycerol alkyd	10	10	10	10	10	10	10	10	10	10	10	10	6	1
LO linolenic glycerol alkyd	10	10	10	10	10	10	10	8	9	4	1‡	1‡	1	—
LO eleostearic glycerol alkyd	10	10	10	10	10	10	10	10	10	10	4	4	2	1
SO linoleic glycerol alkyd	10	10	10	10	10	10	10	6	4	1	1	1	1	—
SO linolenic glycerol alkyd	10	10	10	10	10	10	10	4	6	1	1	1	1	—
LO oleic PE alkyd	10	10	10	10	10	10	10	6	4‡	2‡	2‡	2‡	2	1
LO linoleic PE alkyd	10	10	10	10	10	10	10	10	10	4	2‡	2‡	2	1
LO linolenic PE alkyd	10	10	10	10	10	10	10	4	4‡	1‡	1‡	1‡	1	—
SO oleic PE alkyd	10	10	10	10	10	9	4	2	1‡	1‡	1‡	1‡	1	—
Varnish linseed oil	10	10	10	10	9+	9	8	2	2	2	1	1	1	1
Dehydrated castor oil	10	10	10	10	10	10	10	10	10	6	2	2	2	1
Commercial alkyd	10	10	10	10	10	10	10	6	4‡	4‡	2‡	2‡	2	1
Leaded outside white paint	10	10	10	10	10	10	10	10	10	8	4	4	2	2
Lead-free outside white paint	10	10	10	10	10	10	10	10	10	9	8	8	6	4
Commercial enamel	10	10	10	10	10	10	10	10	10	10	10	10	10	2

* Reading at 8 weeks.

† Reading at 11 weeks.

‡ Chalk washing down over mask.

At 9 weeks the only nonchalking paints were those of dehydrated castor oil, LO linoleic and eleostearic glycerol alkyds, LO linoleic PE alkyd, and the three commercial controls. Of these last, the two house paints did not start to chalk until the 11-week inspection, and

TABLE VI-5

Dirt Retention of Pigmented Films on Exterior Exposure

Ratings are on a scale of 10 (no dirt retention) to 1 (strong dirt retention).

	Weeks of exposure													Months		
Compound	1	2	4	5	6	7	9	10	12	15	16	18	29	10	16	20
Trilinolein	6	8	6	8	8	8	8	9	9	9	9	8	9	8	10	10
Trilinolenin	6	8	6	6	8	2	8	8	8	9	9	9	9	8	10	10
Trieleostearin	4	6	6	6	6	8	6	8	8	9	9	9	9	8	10	—
PE oleate*	—	9	9†	9		9‡	9	9				9		(6)	(10)	(10)
PE linoleate	6	8	6	8	8	8	8	8	8	9	9	9	9	9	10	10
PE linolenate	4	9	6	8	8	8	8	8	8	9	9	9	9	—	—	—
PE eleostearate	6	8	6	8	8	6	9	8	9	9	9	9	9	8	10	10
DiPE oleate*	—	9	9†	9		9‡	9	9				9		(8)	(10)	(10)
DiPE linoleate	6	8	8	8	9	8	8	9	9	9	9	9	9	9	10	10
DiPE linolenate	4	9	6	8	8	8	8	8	8	9	9	9	9	—	—	—
LO linoleic glyc. alkyd	4	4	4	4	2	2	1	2	2	2	2	2	4	6	10	10
LO linolenic glyc. alkyd	6	4	4	4	8	4	6	4	4	6	6	6	6	8	—	—
LO eleostearic glyc. alkyd	6	6	4	6	6	4	4	6	6	6	6	6	6	6	10	10
SO linoleic glyc. alkyd	6	6	4	6	6	6	6	8	6§	8	8	8	8	—	—	—
SO linolenic glyc. alkyd	6	6	4	6	4	4	6	6	6	6	6	6	9	—	—	—
LO oleic PE alkyd	6	8	6	8	8	8	8	8	8	9	9	9	9	8	10	10
LO linoleic PE alkyd	6	6	4	6	4	4	4	4	4	6	6	6	6	8	9	10
LO linolenic PE alkyd	6	6	4	8	4	4	4	4§	4§	4§	4	4	—	—	—	—
SO oleic PE alkyd	8	9	8	9	9	9	9	8§	8§	8	8	8	9	—	—	—
Varnish linseed oil	6	6	4	6	6	4	6	4	6	6	6	6	8	6	10	10
Dehydrated castor oil	4	6	4	4	4	4	4	2	2	4	4	6	6	6	10	10
Commercial alkyd	4	6	4	4	6	6	6	6	6	8	8	8	8	6	10	10
Leaded outside white paint	2	4	2	2	2	2	1	2	2	4	4	4	8	8	9	10
Lead-free outside white paint	2	4	4	4	4	2	1	4	4	4	4	4	6	8	10	10
Commercial enamel	2§	4§	4§	2§	2§	2§	1§	2§	2	2	2	2	2	2	2	6

* Since PE and diPE oleates were put out 7 weeks later than the other compounds, the last three readings for each represent exposures 7 weeks less than the indicated periods.

† Reading at 3 weeks.

‡ Reading at 8 weeks.

§ Mottled dirt.

the commercial enamel did not start for 15 months; whereas of the pure liquid paints, LO linoleic glycerol alkyd alone resisted chalking for 16 weeks, only to develop it badly in a few more weeks. The commercial lead-containing paint showed considerably more chalk as time went on than the lead-free one; at 20 months their respective ratings were "excessive" and "bad."

Dirt retention (Table VI-5) was in approximately inverse order to chalking, as might be expected.

TABLE VI-6

Blistering, Cracking, Peeling, Scaling of Pigmented Films on Exterior Fxposure

	Weeks of exposure											Months			
Compound	2	5	6	7	9	10	12	13	14	15	16	10	13	16	20
Trilinolein	Bl														
Trilinolenin		Bl	Bl	Bl	Bl		P	P	P	P		P-2	S-6	S-4	S
Trieleostearin												P-9	S-8	P-4	P-2
PE oleate															
PE linoleate															
PE linolenate	Bl			IC	Bl	P						P-1	P-1	P-1	P-1
PE eleostearate													S-8	P-6	S-2
DiPE oleate															
DiPE linoleate															
DiPE linolenate							P	P	P	P		P-2	P-1	P-1	P-1
LO linoleic glyc. alkyd												P	P-2	P-2	P-2
LO linolenic glyc. alkyd		F	F	F	F	F	F	F	F	F		P-2	P-1	P-1	P-1
LO eleostearic glyc. alkyd												P-9	P-9	P-8	P-8
SO linoleic glyc. alkyd												P-1	P-1	P-1	P-1
SO linolenic glyc. alkyd			F		F		F	P	F	F		P-2	P-1	P-1	P-1
LO oleic PE alkyd															
LO linoleic PE alkyd												P-9	P-9	P-6	S-2
LO linolenic PE alkyd											IP	P-1	P-1	P-1	P-1
SO oleic PE alkyd												P-1	P-1	P-1	P-1
Varnish linseed oil															
Dehydrated castor oil															
Commercial alkyd													P-9	P-9	P-9
Leaded outside white paint															
Lead-free outside white paint															
Commercial enamel															

Key: Bl, blistering; C, cracking; F, fissures; I incipient; P, peeling (P-9, slight peeling; P-1, panel bare owing to peeling); S, scaling.

Table VI-6 records the blistering, peeling, scaling, and splitting failures of the films, differentiated by letters.

On two panels, blisters developed after only 2 weeks: trilinolein and PE linolenate. Two large blisters present in the trilinolein early in the exposure did not keep the paint from adhering to the glass throughout the 20 months. A large blister full of water in the lower portion of the PE linolenate film was ascribed to water seepage through a minute hole left by the Interchemical gauge. It disappeared in a short time and a spot of aluminum paint was brushed over the area to protect it from further seepage. The gauge marks on all other films were touched up at the same time.

Severe peeling of the paints, resulting either from blisters or from splitting of the films, was evident in five cases after from 9 to 15 weeks: those containing PE and diPE linoleate, trilinolenin, and the long-oil and short-oil linolenic glycerol alkyds. The only ones that came through the whole 20 months with practically no blistering were the ones containing linseed and dehydrated castor oils, trilinolein, PE and diPE linoleate, PE and diPE oleate, LO oleic glycerol alkyd, and the three commercial products.

General exposure comparisons may be made as follows from the data shown in Tables VI-2, VI-4, VI-5, and VI-6. All the pure-compound paints weathered more poorly on glass than those made from the three commercial liquids, which in turn performed less well than the three commerical coatings. Peeling was worse for the linolenic esters and alkyds than for those containing linoleic acid, and the eleostearic compounds were intermediate.

A brief comparison of the clear and pigmented films for each individual vehicle, to bring out the influence of pigmentation, follows:

Trilinolein, clear, tacky 13 weeks; pigmented, dry overnight. Both failed by erosion.

Trilinolenin, clear, crawled but dried better than pigmented, and weathered better, though both lost most of the film by peeling and scaling.

Trieleostearin, both appeared dry in 24 hours but were tacky when exposed. Clear wrinkled badly in drying, eroded; pigmented peeled.

PE oleate, clear, never dried enough to expose; pigmented took 7 weeks, failed by erosion.

PE linoleate, like trilinolein. Clear, tacky; pigmented dried well. Both failed by erosion.

PE linolenate, both crawled, but dried in 24 hours. Clear eroded with some peeling; pigmented peeled badly.

PE eleostearate, both dried very fast; clears, badly wrinkled, washed off slowly; pigmented scaled.

DiPE oleate, same as PE oleate.

DiPE linoleate, clear crawled badly, but the large droplets adhered and weathered well. Pigmented formed satisfactory films, also weathered well except for pitting to the surface of the glass.

DiPE linolenate, both tended to crawl, dried overnight. Clear eroded and flaked; pigmented adhered poorly.

LO linoleic glycerol alkyd, clear and pigmented dried well, but all films peeled early.

LO linolenic glycerol alkyd set up in a few hours, dried overnight; adhesion poor like the preceding, all films peeled off in about 9 months.

LO eleostearic glycerol alkyd, both dried fast. Clear peeled off in 9 months; pigmented good at 20 months with some peeling and pitting to the glass.

SO linoleic and linolenic glycerol alkyd films all tended to crawl; they dried overnight and peeled badly, none adhering at 9 months.

LO oleic PE alkyd, both crawled, both tacky at exposure (clear to about the 15th week), both adhered throughout the 20 months but clear developed spotty, frosty appearance, some shrinking and blistering; pigmented developed some erosion, separation from glass, pitting to the glass.

LO linoleic PE alkyd, both dried in 24 hours; clear developed frosty appearance, shrank and blistered slightly worse than oleic; pigmented scaled owing to poor adhesion and brittleness.

LO linolenic PE alkyd, and SO oleic PE alkyd: all four dried well, but all peeled off in less than 9 months.

Varnish linseed oil, clear, took weeks to dry; pigmented, dried overnight. Both failed mainly by erosion rather than peeling.

Dehydrated castor oil, clear, was tacky as long as the linseed oil; pigmented, a few weeks. Failure of both by erosion.

Commercial alkyd, both dried well; clear blistered and peeled badly, pigmented peeled and separated from glass, though tough.

Photographs of films at intermediate and final stages of exposure appear in Figs. VI-3 to VI-18.

Although the results obtained on this project tied in generally with those of the others, they were not for the most part amenable to statistical analysis nor to direct correlation. An exception to this statement is found in the fact that the degree of chalking and erosion noted in this project corresponded closely with the amount of zinc oxide pigment leached from the pigmented films in Project 17 (Chapter VII) on the chemical analysis of films at different stages of accelerated exposure.

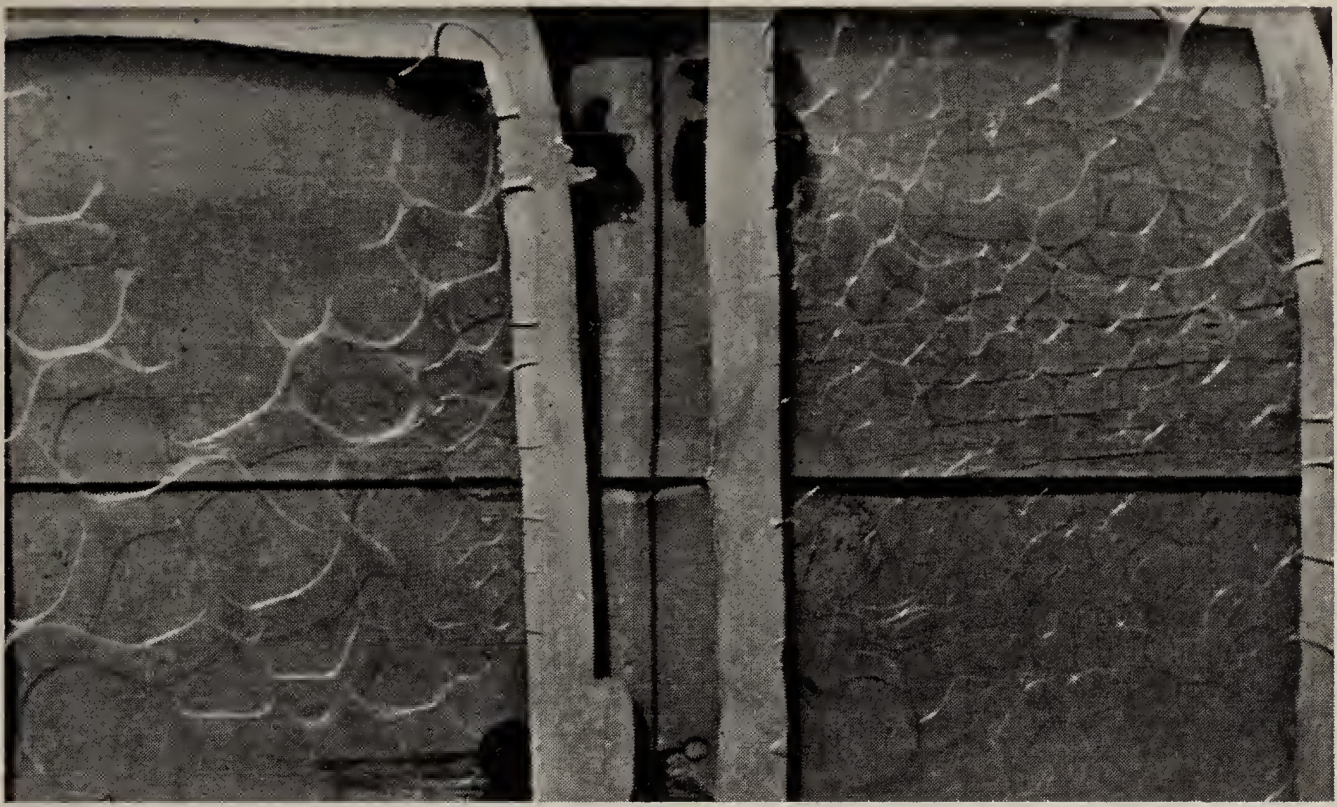

Fig. VI-3. Clear LO linolenic glycerol alkyd, exposed 19 weeks, showing "poultry-netting" wrinkled effect.

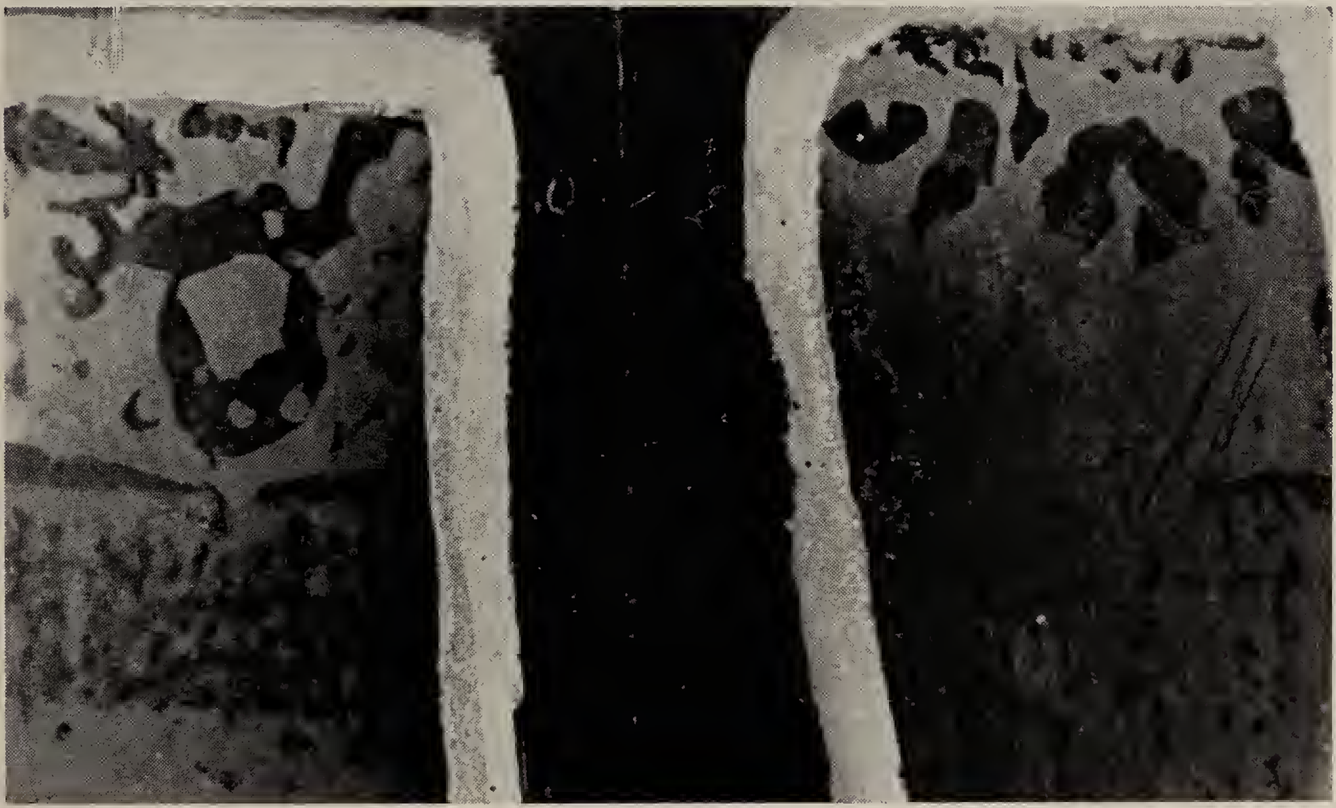

Fig. VI-4. Clear trilinolenin, exposed 20 months.

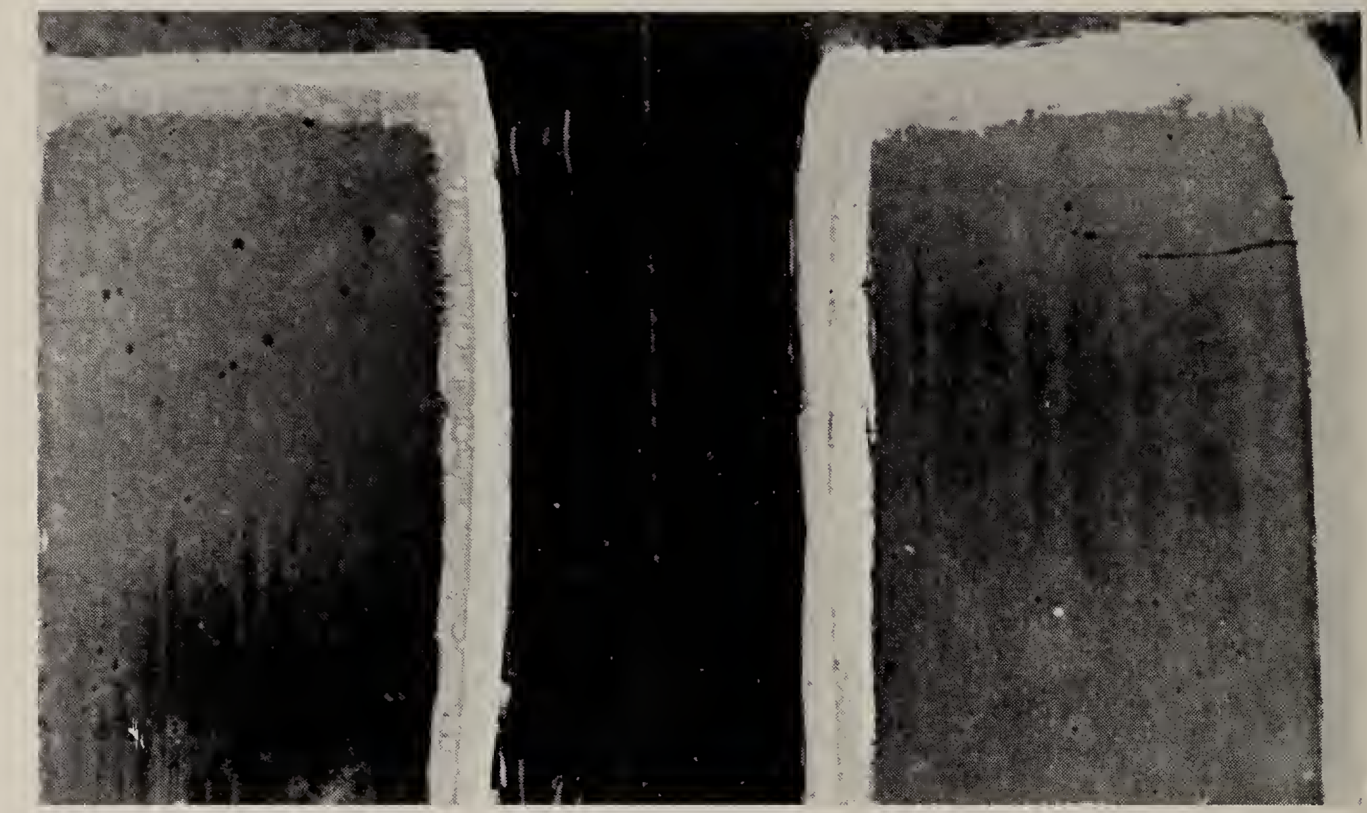

Fig. VI-5. Clear PE eleostearate, exposed 20 months.

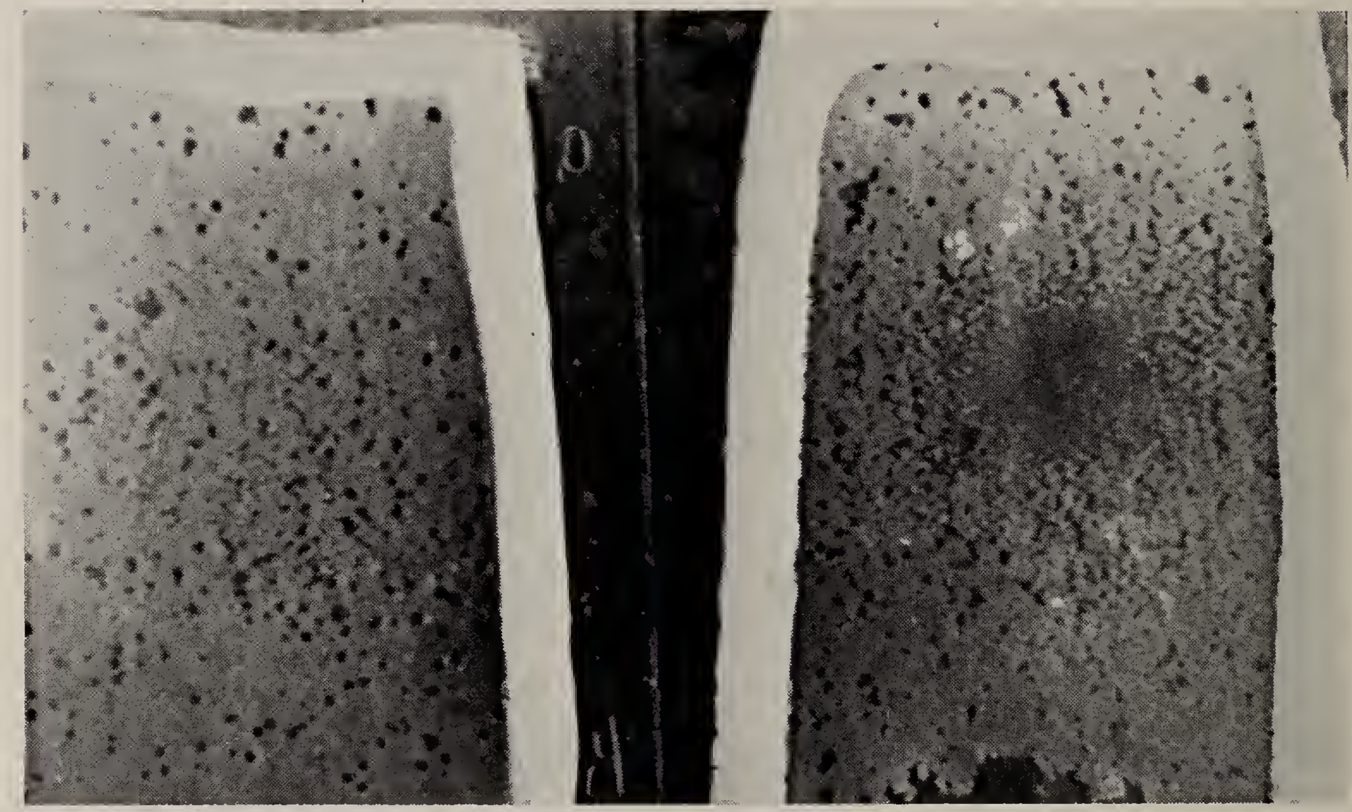

Fig. VI-6. Clear diPE linolenate, exposed 20 months.

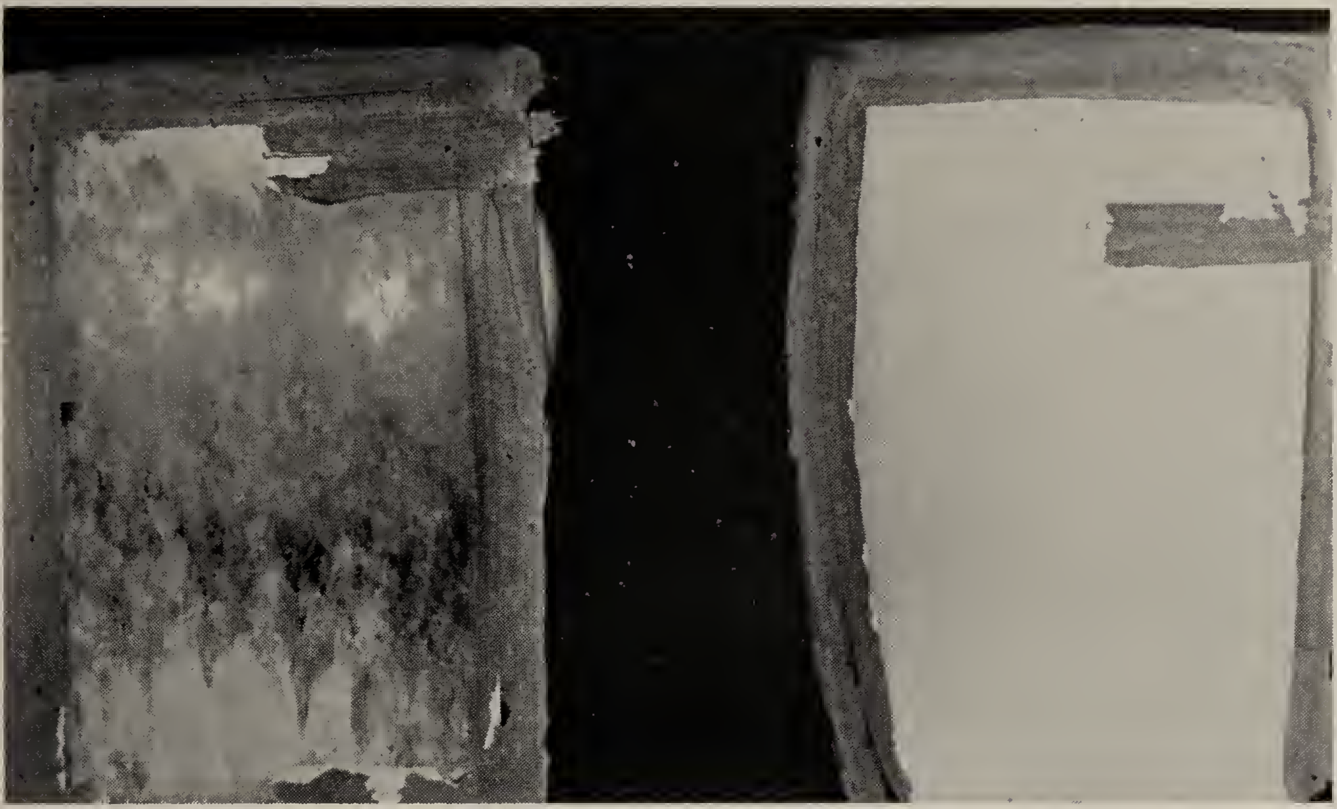

Fig. VI-7. Pigmented trilinolein, exposed 20 months.

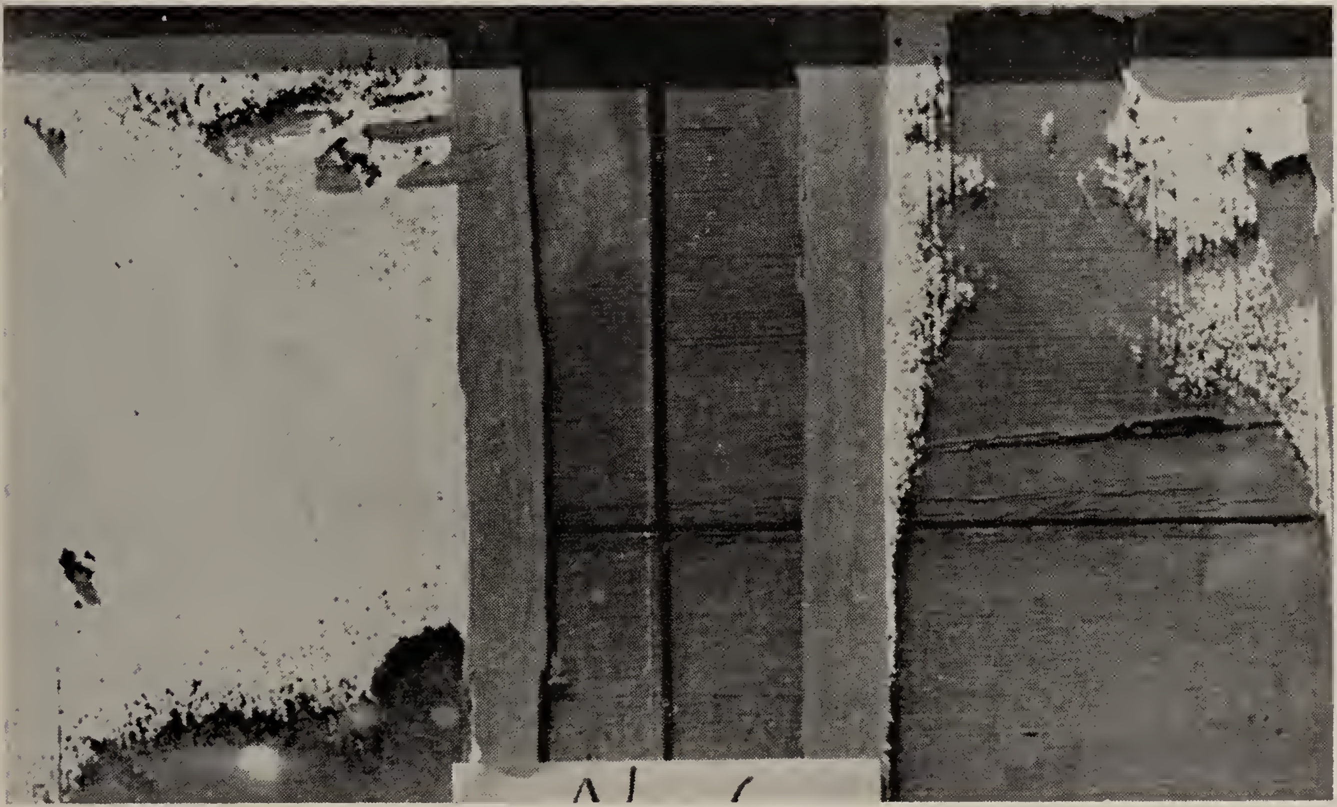

Fig. VI-8. Pigmented trilinolenin, exposed 20 months.

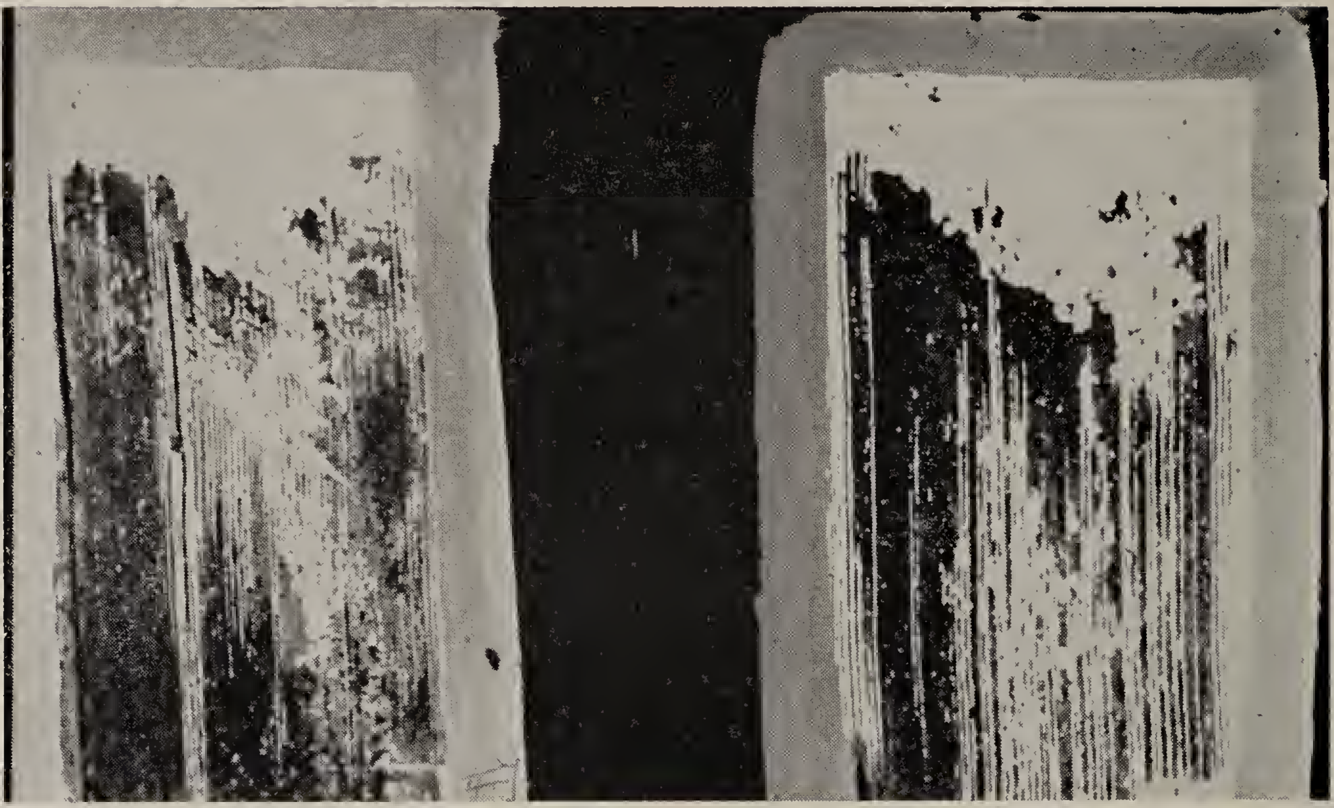

Fig. VI-9. Pigmented PE eleostearate, exposed 20 months.

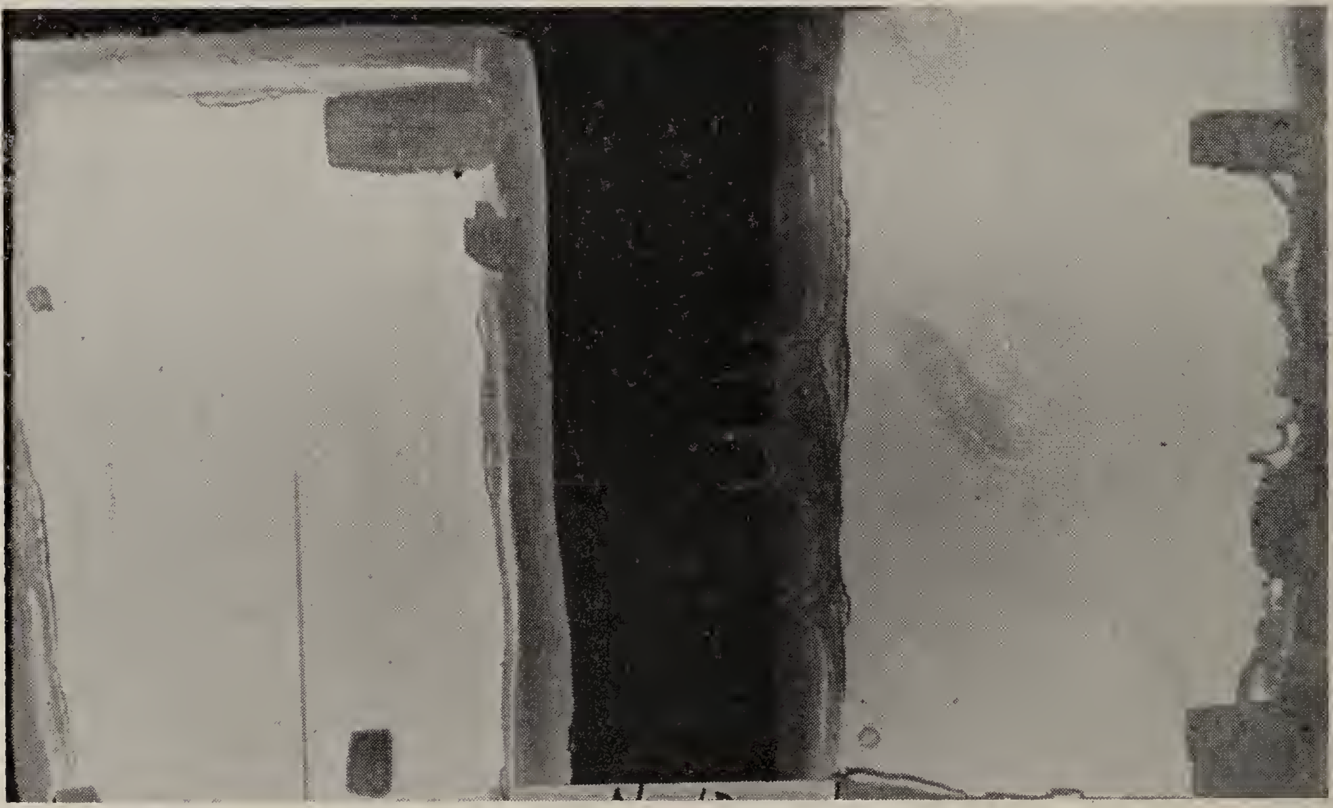

Fig. VI-10. Pigmented diPE oleate, exposed 18 months, 1 week (80 weeks).

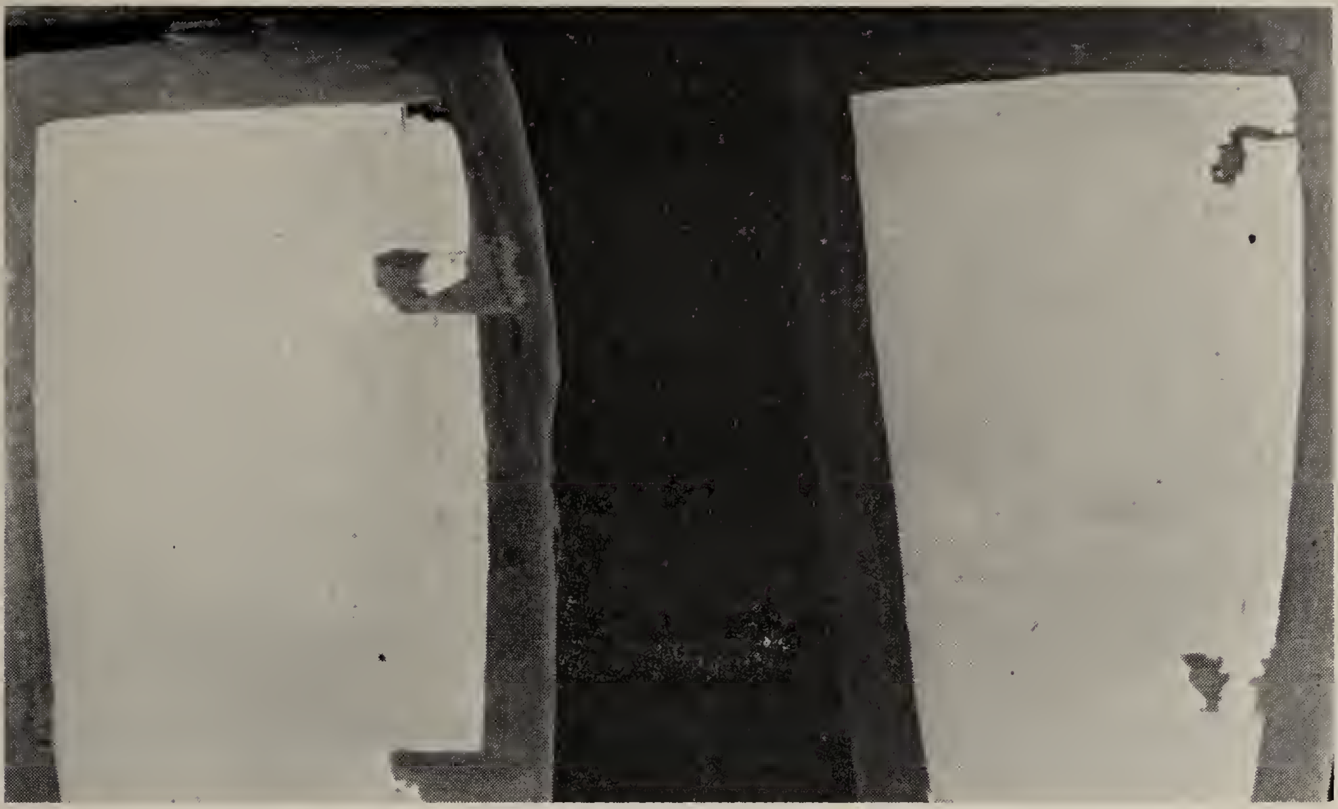

Fig. VI-11. Pigmented diPE linoleate, exposed 20 months.

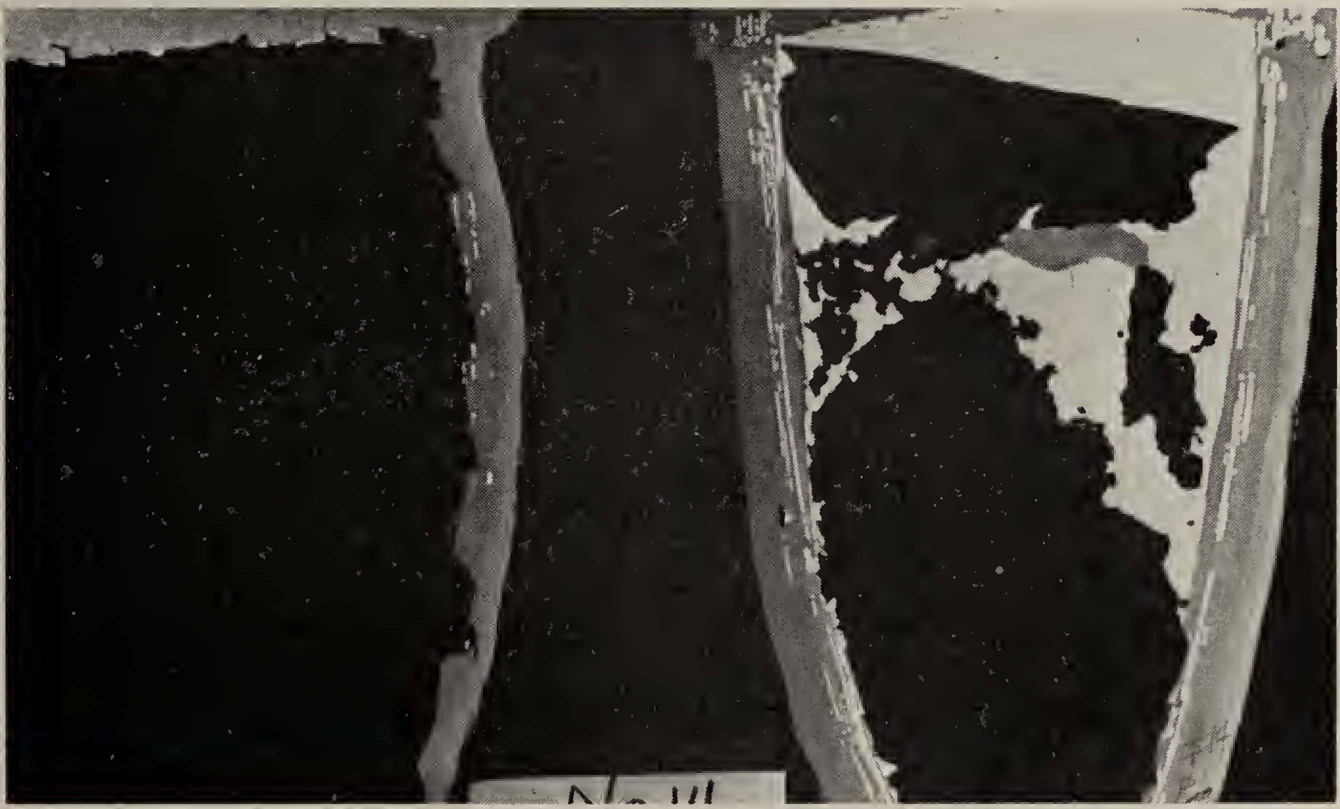

Fig. VI-12. Pigmented LO linoleic glycerol alkyd, exposed 20 months.

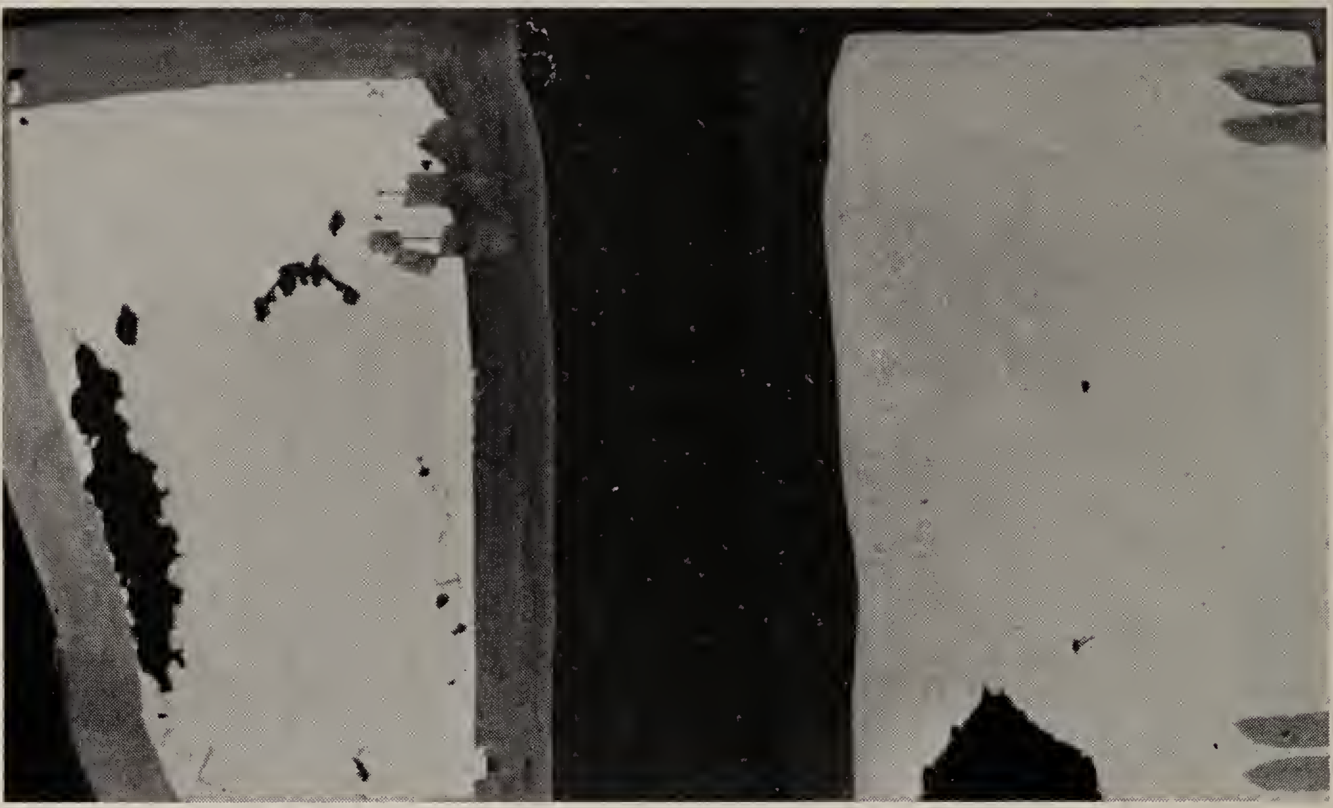

Fig. VI-13. Pigmented LO eleostearic glycerol alkyd, exposed 20 months.

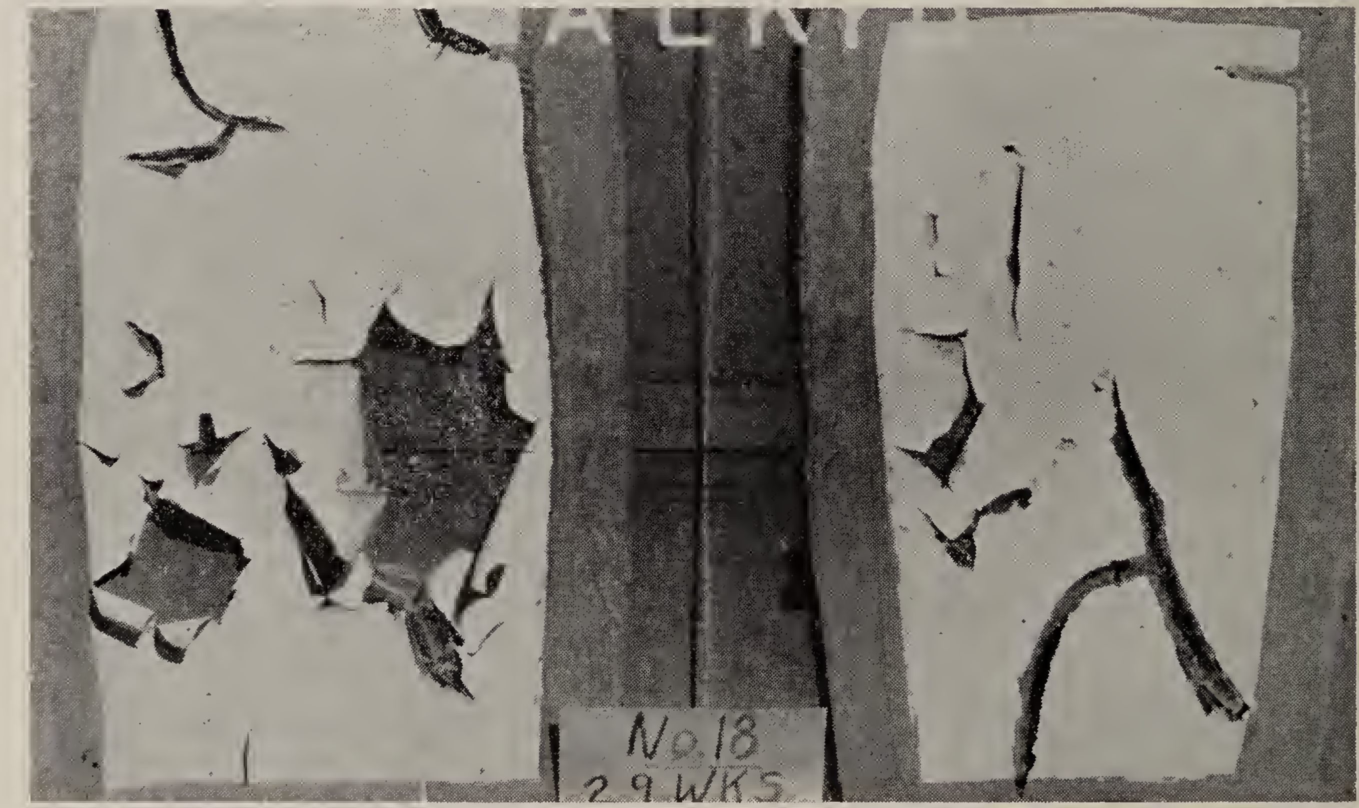

Fig. VI-14. Pigmented SO linolenic glycerol alkyd, exposed 29 weeks.

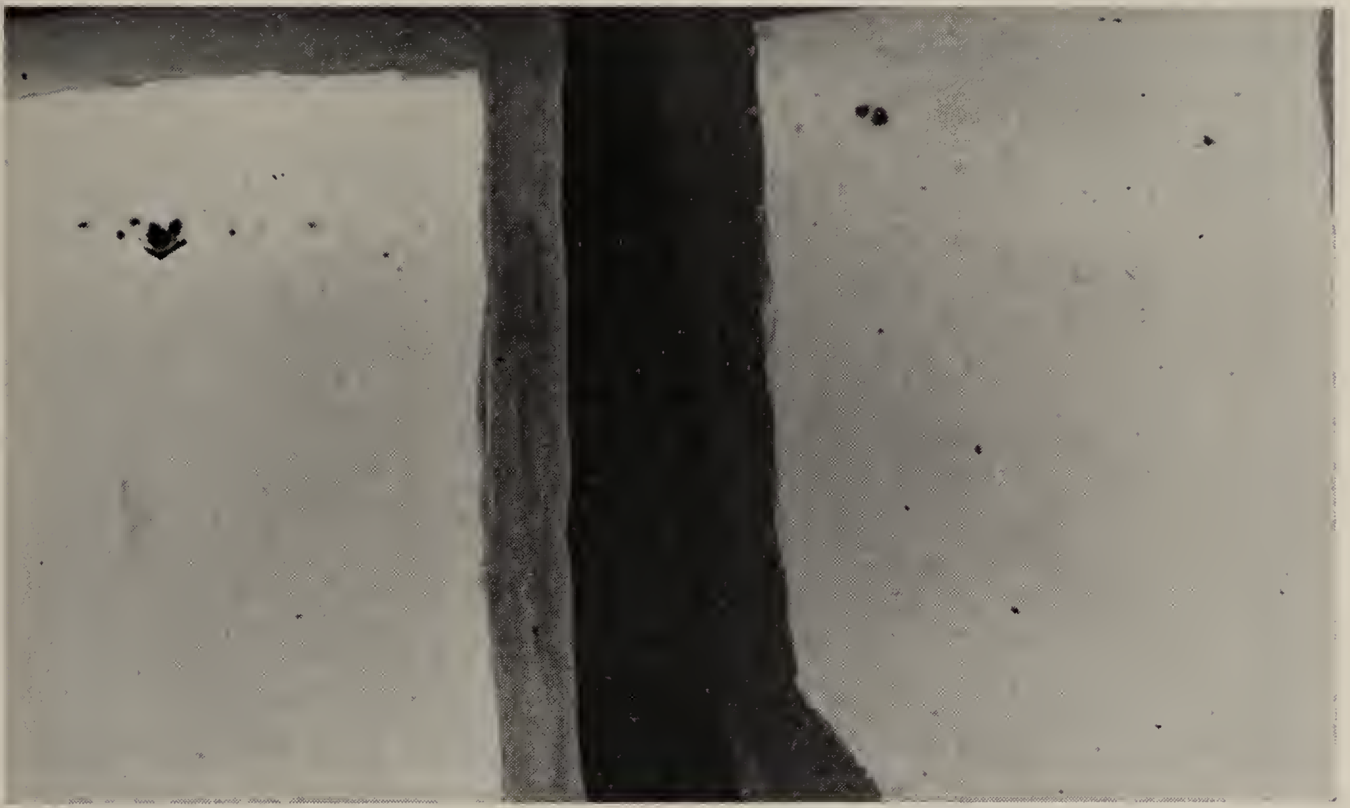

Fig. VI-15. Pigmented LO oleic PE alkyd, exposed 20 months.

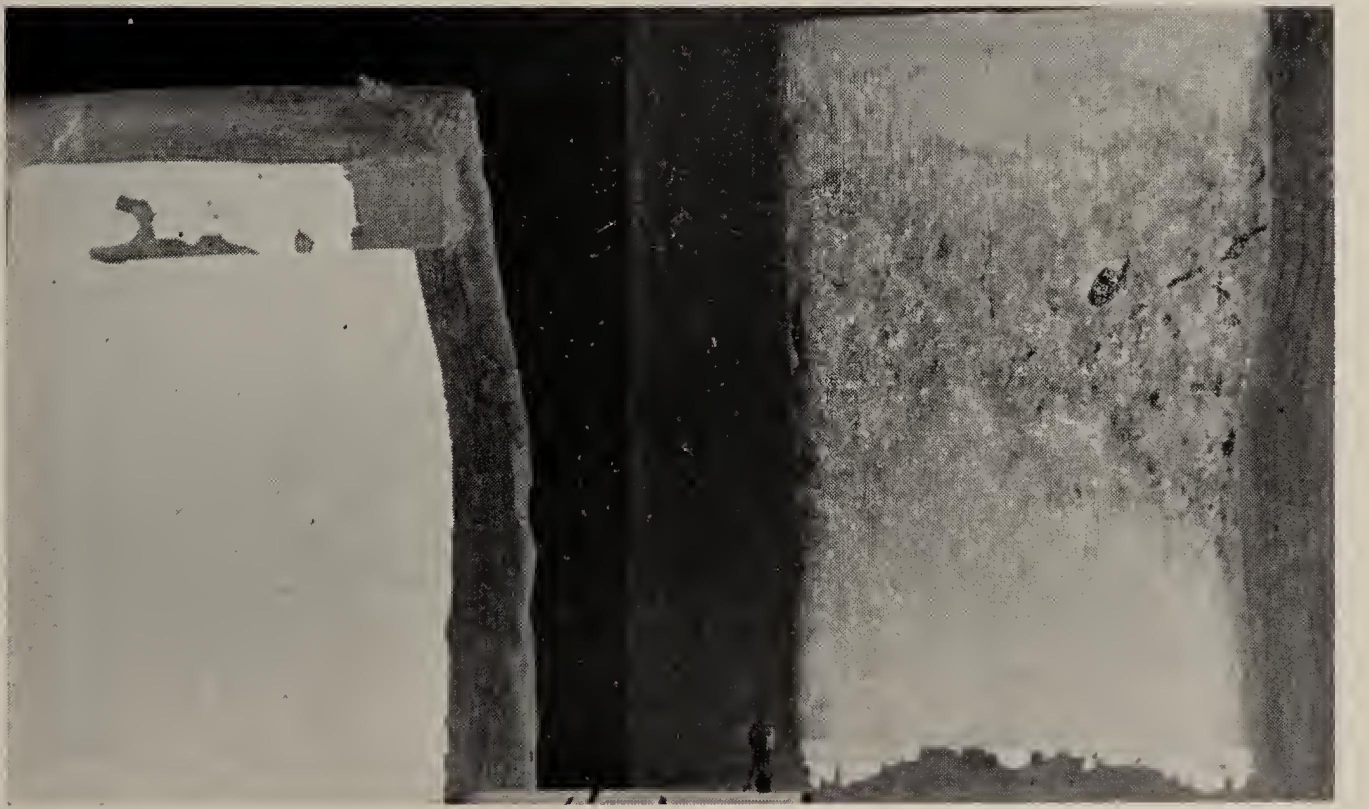

Fig. VI-16. Pigmented varnish linseed oil, exposed 20 months.

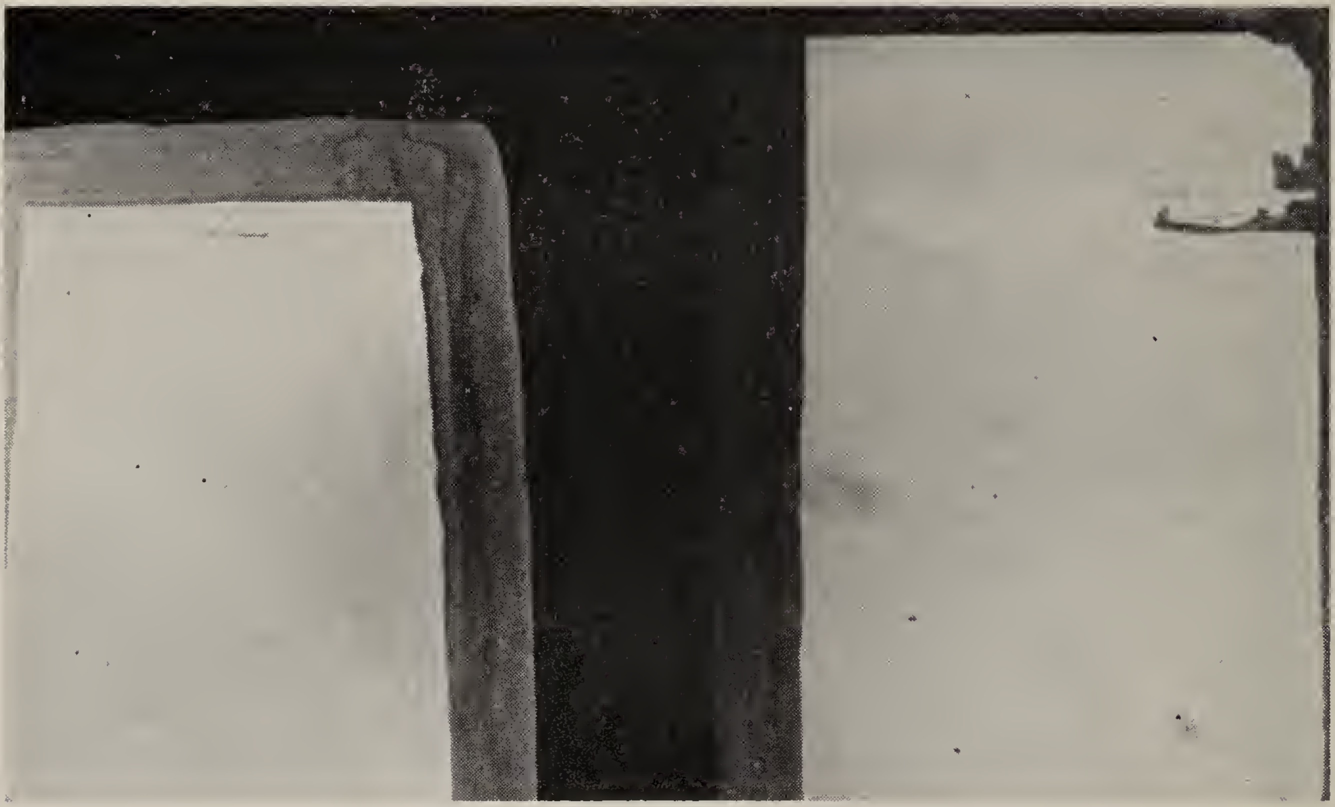

Fig. VI-17. Pigmented dehydrated castor oil, exposed 20 months.

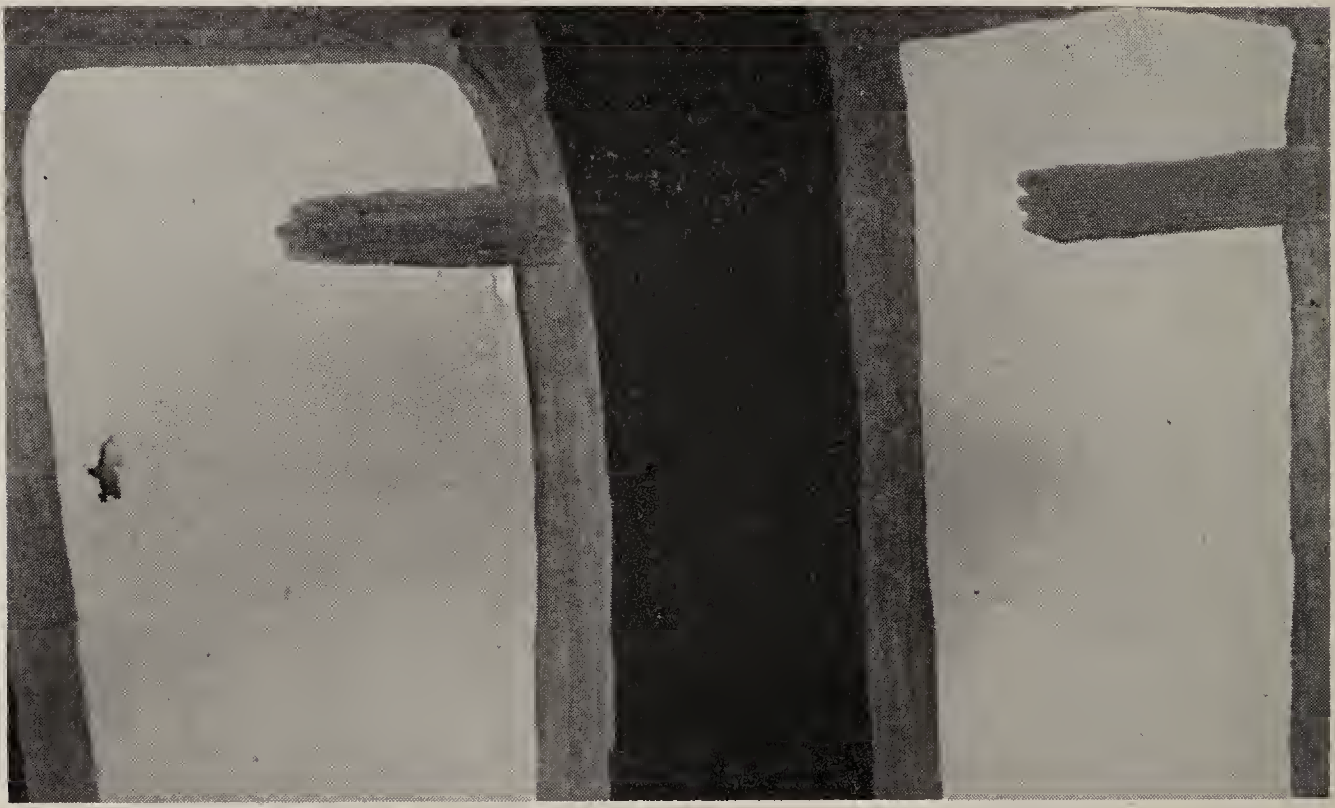

Fig. VI-18. Pigmented commercial alkyd, exposed 20 months.

CHAPTER VII

Accelerated Weathering Tests, Hardness and Abrasion Resistance, Chemical Changes, Refractive Index

As was mentioned in the preceding chapter, accelerated exposure tests formed part of the studies of two cooperating groups, and their data are presented here for ready comparison with the outdoor exposure results. These groups at the same time studied other changes in properties of aging films. Their reports on these are most conveniently included and discussed in this chapter.

Rate of Erosion of Clear and Pigmented Films, Project 13—Southern Club

The purpose of this project was to determine the rate of surface wear of films under accelerated weathering conditions, and also to measure, quantitatively if possible, the screening effect of pigments in protecting the film and decreasing the erosion rate. The project was carried out by Ewin B. Kiser, Jr., under the supervision of Dr. J. H. Coulliette at the Industrial Research Institute of the University of Chattanooga, Tennessee. Raymond C. Adams of the Southern Club not only gave it his close attention but arranged for the use of Gilman Paint and Varnish Co.'s Weather-Ometer,* an Atlas Twin Arc Machine, Model DL-TS. Mr. Adams presented a preliminary report on this Project and Project 22 at the 1951 annual meeting of the Southern Club (*Official Digest,* No. 315, 218 (April, 1951)). The complete report appeared in the *Official Digest,* No. 322, 724 (November, 1951), as by "Ewin B. Kaiser" and J. H. Coulliette.

Plate glass panels, $^1/_8$ inch thick, 9 × 12 inches, were used. Before cleaning, they were laid off and scored with a glass cutter on the underside so that pieces of suitable size for the exposure tests and for hardness and abrasion tests could be readily obtained by breaking along the scored lines. The cleaning cycle included the usual nitric-sulfuric acid treatment and rinsing with 5% alcoholic benzoic acid solution, followed by rinsing, drying, and polishing with a chamois skin.

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* Registered trade name of Atlas Electric Devices Co., Chicago.

The ampules containing the 23 clear and 23 pigmented samples were stored in a refrigerator until opened. Materials were then diluted if too viscous, and treated with the standard drier. The mixed sample was stored under nitrogen for 48 hours.

Films were applied on duplicate panels by means of a 6-inch Baker blade with motor drive, and the film thickness was measured by the Interchemical gauge; if correct thickness was not obtained on the first draw-down, the blade was readjusted for the second one. Tables VII-1, 2, 3, and 4 show wet film thickness data, drying times, and film characteristics for the clear and pigmented compounds. The panels were placed on an accurately leveled table and dried in a room held at 77° F. and 50% humidity with constant air circulation. After 7 days drying, the plate on which the thickness of film for each sample was nearer to the desired value, was broken into smaller panels for the various tests; the other plate was not used. Duplicate films were placed one above the other in the Weather-Ometer. The equipment was operated for 115 hours per week, and observations were made weekly of thickness, weight, gloss, and appearance (chalking, etc.). At each removal from the Weather-Ometer, panels were wiped free of loose material and dried.

Thickness measurements were made with a micrometer caliper at four positions marked by circles scratched on the underside of the glass. In most cases no appreciable reduction in thickness was noted over several weeks; in others, checking, cracking, and wrinkling made accurate measurement impossible. Accordingly, no numerical thickness data were reported.

Weight losses were taken on an analytical balance, using the average for the two panels. The upper panel usually lost slightly more than the lower one.

Gloss was measured with a Hunter Color and Color Difference Meter according to ASTM specifications for 60° specular gloss. Some of the clear films gave initial readings above the "100" mark on the

TABLE VII-1
Film Thickness, Drying Time, Film Character of Clear Compounds

	Wet film thickness (mils)				
Compound	Required	Blade setting	Obtained	Setting time	Condition of film obtained
Trilinolein	1.25	2.0	1.2	36 hr.	Tacky at 8 wk.
Trilinolenin	1.25	2.0	1.3, 1.2	6 hr.	Very bad crawling
PE oleate	1.25	1.8	1.3	—	Still wet at 2 mo.
PE linoleate	1.25	2.0	1.0, 1.8	5 hr.	Slightly tacky at 1 wk.
PE linolenate	1.25	2.0 2.5	1.0 2.2	3.5 hr.	Crawled badly, fine wrinkles
PE eleostearate	1.25	2.0	1.3, 1.4	3 hr.	Tiny wrinkles all over
DiPE oleate	1.25	1.6	1.2, 1.3	2 mo.	Crawled very badly
DiPE linoleate	1.25	1.8 1.9	1.1 1.3	O.N.*	Very bad crawling
DiPE linolenate	1.25	2.0 1.9	1.5 1.4	4 hr.	Formed pool in center of panel
LO linoleic glyc. alkyd	3.0	4.0	3.0, 3.1	O.N.*	Good
LO linolenic glyc. alkyd	3.0	4.5	2.8, 3.0	1 hr.	Good
LO eleostearic glyc. alkyd	3.0	4.5	3.0–3.1, 3.5	2 hr.	Good
SO linoleic glyc. alkyd	2.98	5.0	3.0	O.N.*	Fair
SO linolenic glyc. alkyd	3.2	4.5	3.0, 3.2	O.N.*	Fair
LO oleic PE alkyd	3.0	4.0	2.9–3.1	2 wk.	Tacky after 5 wk.
LO linoleic PE alkyd	3.0	4.0	2.1, 3.0	O.N.*	Slightly grainy
LO linolenic PE alkyd	3.0	4.0	2.9–3.0 3.0–3.4	2.5 hr.	Thin consistency
SO oleic PE alkyd	3.08	5.2	3.0, 2.8	45 min.	Good
Varnish linseed oil	1.25	2.0	1.1	6 hr.	Tacky after 11 wk.
Dehydrated castor oil	1.33	2.2 2.0	1.5 1.1	3 hr.	Slightly tacky at end of 1 wk.
Commercial alkyd	3.2	5.0 4.0	3.1 3.0	3.5 hr.	Good

* O.N.—overnight.

instrument; these are recorded as 100. Values for clear films at various elapsed times appear in Table VII-5 and for pigmented in Table VII-6.

TABLE VII-2

Film Thickness, Drying Time, Film Character of Pigmented Compounds

Compound	Wet film thickness (mils)			Setting time	Condition of film obtained
	Required	Blade setting	Obtained		
Trilinolein	2.7	3.8	2.8	O.N.*	Good
Trilinolenin	2.42	3.5	2.4	O.N.*	Small flakes, as of pigment, in film
Trieleostearin	3.2	5.0 4.5	4.5 3.0	4 hr.	Specky, stringy, trace tackiness at 1 wk.
PE oleate	2.86	4.5 4.3	3.2 2.8	21 days	Not fully dry at 2 mo.
PE linoleate	2.92	4.0	2–5–3.0	O.N.*	Good
PE linolenate	2.78	3.9	2.8–2.9	O.N.*	Good
PE eleostearate	2.9	4.7	3.2–2.9	4 hr.	Contained specks and skins
DiPE oleate	3.1	4.6 4.8	3.0 3.1	17 days	Not fully dry at 2 mo.
DiPE linoleate	2.98	4.9	3.2	O.N.*	Stringy
DiPE linolenate	2.61	3.7	2.7–2.6	O.N.*	Grainy
LO linoleic glyc. alkyd	3.55	5.5	3.6–3.8	O.N.*	Thin consistency
LO linolenic glyc. alkyd	3.55	6.2 6.1	3.9 4.0	O.N.*	Good
LO eleostearic glyc. alkyd	5.72	9.5	5.7–5.8, 5.9	70 min.	Good
SO linoleic glyc. alkyd	3.97	6.5	4.0	50 min.	Good
SO linolenic glyc. alkyd	3.62	5.5	3.7	50 min.	Good
LO oleic PE alkyd	3.55	5.1	3.5	9 days	Tacky after 2 mo.
LO linoleic PE alkyd	3.55	5.1	3.5–3.7	O.N.*	Water-thin consistency
LO linolenic PE alkyd	3.55	5.8	3.6	2 hr.	Water-thin consistency
SO oleic PE alkyd	4.57	7.0	4.5–4.6	25 min.	Good
Varnish linseed oil	2.17	3.5 3.2	2.3 2.2	8 hr.	Good
Dehydrated castor oil	2.60	4.0	2.6	3 hr.	Slightly striated
Commercial alkyd	3.63	6.0	3.6	2 hr.	Good

* O.N.—overnight.

TABLE VII-3

Wet Film Thickness in Mils of Films for Erosion, Hardness, and Abrasion Studies

	Fatty acid component							
	Oleic		Linoleic		Linolenic		Eleostearic	
Type vehicle	Clear	Pigmented	Clear	Pigmented	Clear	Pigmented	Clear	Pigmented
Glyceryl ester			1.2	2.8	1.25	2.4	—	3.75
PE ester	1.3	3.0	1.4	2.75	1.6	2.85	1.35	3.05
DiPE ester	1.25	3.05	1.2	3.2	1.45	2.65		
LO glycerol alkyd			3.05	3.7	2.9	3.95	3.3	5.8
SO glycerol alkyd			3.0	4.0	3.1	3.7		
LO PE alkyd	3.0	3.5	2.55	3.6	3.1	3.6		
SO PE alkyd	2.9	4.55						

Varnish linseed oil		Dehydrated castor oil		Commercial alkyd	
Clear	Pigmented	Clear	Pigmented	Clear	Pigmented
1.1	2.25	1.3	2.6	3.05	3.6

TABLE VII-4

Set-to-Touch Time in Hours of Films for Erosion, Hardness, and Abrasion Studies

	Fatty acid component							
	Oleic		Linoleic		Linolenic		Eleostearic	
Type vehicle	Clear	Pigmented	Clear	Pigmented	Clear	Pigmented	Clear	Pigmented
Glyceryl ester			36	16—*	6	16—*	—	4
PE ester	†	504	5	16—*	3.5	16—*	3	4
DiPE ester	1440	408	16—*	16—*	4	16—*		
LO glycerol alkyd			16—*	16—*	1	16—*	2	1+ (70 min.)
SO glycerol alkyd			16—*	1—	16—*	1—		
LO PE alkyd	336	216	16—*	16—*	2.5	2		
SO PE alkyd	0.75	0.5						

Varnish linseed oil		Dehydrated castor oil		Commercial alkyd	
Clear	Pigmented	Clear	Pigmented	Clear	Pigmented
6	8	3	3	3.5	2

* Dried overnight.

† Did not set to touch at end of two months.

TABLE VII-5
Gloss of Clear Compounds

Compound	Accelerated exposure periods (115 hr. each)														
	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28
Trilinolenin	100+	77	58	35	23	32	32	41	47	48	44	42			
PE linoleate	100+	63	56	45	36	29	27	26	28	25	34	35			
PE linolenate	100+	100+	80	59	49	34									
PE eleostearate	15	12	14	14	10	9	11	11	11	10	12	13	18		
DiPE linoleate	100+	81	52	55	34	30	35								
DiPE linolenate	100+	100+	93	55	40	26	24	21	19	17	17				
LO linoleic glycerol alkyd	100+	100+	100+	92	56	41	38	25	20	17					
LO linolenic glycerol alkyd	100+	100+	99	50											
LO eleostearic glycerol alkyd	100+	100+	100+	81	56	53									
SO linoleic glycerol alkyd	100+	100+	100+	100+	87	70	63	53	45	40	34	36	29	12	
SO linolenic glycerol alkyd	100+	100+	96	74	72	68	61								
LO oleic PE alkyd	100+	94	77	62	60	47	47	44	35	30	30				
LO linoleic PE alkyd	100+	100+	100	83	55	53	46	38							
LO linolenic PE alkyd	100+	100+	100+												
SO oleic PE alkyd	100+	100+	100+	100+	95	79	75	69	61	59	60	61	56	48	
Dehydrated castor oil	100+	87	69	54	42	34	26	20	15	15	13	11	11	11	
Commercial alkyd	100+	100+	100+	95	80	55	50	44	46	34	34	29	24	19	

TABLE VII-6

Gloss of Pigmented Compounds

Compound	Accelerated exposure periods (115 hr. each)																				
	0	2	4	6	8	10	12	14	16	18	20	22	24	26	28	30	32	34	36	38	40
Trilinolein	2	1	0.9	0.6	0.7	0.6															
Trilinolenin	27	0.6	0.6	0.5	0.6	0.8															
Trieleostearin	2	0.2	0.5	1																	
PE linoleate	3	2	2	2	2	2															
PE linolenate	8	0.8	2	3	1																
PE eleostearate	0.6	0.4	0.5	0.6	0.8	0.3															
DiPE linoleate	1	0.3	0.3	1	0.6																
DiPE linolenate	13	2	2	2	2																
LO linoleic glycerol alkyd	79	47	39	35	28	20	17	22	19	16	16	13	11	10							
LO linolenic glycerol alkyd	84	46	38	35	27																
LO eleostearic glycerol alkyd	7	4	4	5	3	3	3	2	2	2	2	3	3								
SO linoleic glycerol alkyd	79	44	39	36	28	25	25	28	27	25	24	26	24	23	25						
SO linolenic glycerol alkyd	88	39	36	48	25	17	4														
LO linoleic PE alkyd	40	14	14	13	7	6	4	2													
LO linolenic PE alkyd	92	64	54	30																	
SO oleic PE alkyd	24	20	18	14																	
Varnish linseed oil	4	3	2	2	2	2	0.8														
Dehydrated castor oil	34	7	6	6	6	5	5	4	4	4	4	3	3	5	4						
Commercial alkyd	35	19	14	15	14	14	13	13	12	11	10	10	10	11	10	10	10	10	9	9	9

Chalking as noted each week was described as very slight, slight, medium, heavy, or very heavy. With one exception, panels were retained in the Weather-Ometer until failure, which was defined as the condition when, owing to erosion, the film no longer provided efficient protection for the underlying surface; the longest exposure was 44 weeks, for the pigmented commercial alkyd, which still gave no indication of failure at that time.

The samples of SO eleostearic glycerol alkyd, both clear and pigmented, and of clear trieleostearin gelled in the ampules either before opening or during the aging period, and could not be used; and failure to dry within a reasonable time prevented exposure tests on the pigmented PE and diPE oleates and LO oleic PE alkyd, and on the clear linseed oil, trilinolein, PE and diPE oleates. The pigmented samples of trieleostearin and LO linoleic PE alkyd had to be given an additional 7 days to dry before (having then hardened to the same degree as the other materials) they could be put into the Weather-Ometer.

In the following synopsis of the exposure results, C indicates chalking; F, failure; W, general effects of weathering; and the numbers are the weekly exposure periods of 115 hours each.

Clear Compounds

Trilinolenin: cracking and blistering, some peeling around blisters 1, slight wrinkling 3, more peeling and cracking 5, heavy checking and peeling 16, film nearly gone owing to checking and peeling 26.

PE linoleate: wrinkling, blistering, cracking 1, more wrinkling and cracking 3, heavy checking 14, film nearly gone owing to checking and peeling 23.

PE linolenate: peeling along edges 6, small cracks 7, bad peeling 8, excess peeling (removed) 11.

PE eleostearate: slight peeling 1, wrinkling 3, checking 21, test terminated 23.

DiPE linoleate: excessive creacking and peeling 1, checking 2, F due to checking and peeling 12.

DiPE linolenate: slight cracking 2, checking 6, peeling along edges 9, medium checking 10, losing adhesion at edge 15, F due to peeling and checking 20.

LO linoleic glycerol alkyd: very small amount of checking 9, heavy checking 12, cracks 16, F due to checking 18.

LO linolenic glycerol alkyd: considerable peeling at edges 2, top panel removed (half of film peeled off) 5, lower panel removed, completely peeled off 7.

LO eleostearic glycerol alkyd: slight peeling at edges 7, much peeling at edges 8, about three-fifths of film peeled off (removed) 11.

SO linoleic glycerol alkyd: slight blistering 5, slight cracking 7, checking 16, test terminated 31.

SO linolenic glycerol alkyd: slight peeling at edges 4, considerable 5, few tiny holes 8, about two-thirds of film peeled off (removed) 13.

LO oleic PE alkyd: slight blistering 1, checking 10, some loss of adhesion at edges 13, test terminated 25.

LO linoleic PE alkyd: "poultry-netting" cracking 7, checking 9, heavy checking 13, F due to checking 14.

LO linolenic PE alkyd: peeling at edges 3, approximately one-fifth peeled off 4, approximately half peeled off 5, about three-fourths peeled off 7.

SO oleic PE alkyd: good condition (test terminated) 32.

Dehydrated castor oil: small blisters 1, small cracks with slight peeling 5, heavy checking 16, test terminated 30.

Commercial alkyd: small blisters and wrinkles 6, wrinkled surface resembling poultry netting 10, heavy checking 17, test terminated 31.

Pigmented Compounds

Trilinolein: C, very slight 2 increasing gradually to heavy 6, heavy until F.

W, slight pitting 5, checking visible to eye 10, F 12 due to checking and C.

Trilinolenin: C, slight 1, increasing to heavy at F.

W, slight peeling at edges 2, very small holes 4, checking visible under magnifying glass 5, F 10 due to C and checking.

Trieleostearin: C, very slight 2, increasing to heavy at F.

W, very slight pitting 2, heavy checking 8 with some peeling at edges; F 9 due to C, checking, and peeling.

PE linoleate: C, very slight 2, increasing to very heavy at F.

W, few small holes 9; considerable pitting 10; F 11 due to C and checking.

PE linolenate: C, very slight 1, slight from 2 until F.

W, excess peeling around edges (which were then cemented to plate with enamel) 1; visible checking, many small holes and cracks 7; F due to checking, 9.

PE eleostearate: C, very slight 1 increasing to heavy at F.

W, slight checking under magnifying glass, considerable peeling around edges, 9; visible checking 10; F 12 due to checking and peeling.

DiPE linoleate: C, very slight 1, increasing to heavy at 11, heavy until F.

W, slight peeling about edge 2; very slight checking under magnifying glass 9; F due to C, checking, and peeling, upper panel 11, lower 16.

DiPE linolenate: C, very slight 1, slight 3 until F.

W, excess peeling and loss of adhesion (edges cemented to plate with enamel) 1; small cracks 3; F due to checking 9.

LO linoleic glycerol alkyd: C, very slight 11, continuing until F.

W, slight peeling about edges 2, few small cracks, checking 15, more checking, cracking, and peeling 19, F 25 due to checking and peeling around cracks.

LO linolenic glycerol alkyd: C, none.

W, very slight wrinkling 1, peeling around edges, cracks due apparently to shrinkage of film 2, half of film peeled from top panel and several $^1/_4$-inch cracks 7, half of film from lower panel, very bad cracking 8.

LO eleostearic glycerol alkyd: C, slight 8, slight to medium until F.

W, slight peeling about edge 1; excess peeling (edges cemented to panel with enamel) 2; several tiny holes, cracks 17, checking and enlargement of holes 18, F 26 due to checking and peeling.

SO linoleic glycerol alkyd: C, none.

W, slight peeling along edge 2, few small holes 17; panels broken, film in fair condition except few small holes, some peeling at edges 29.

SO linolenic glycerol alkyd: C, sudden medium 11.

W, wrinkling under magnifying glass 1, cracks from shrinkage 2, excess peeling from edges, many $^1/_8$-inch cracks, F, 12.

LO linoleic PE alkyd: C, slight 8 until F.

W, peeling around upper edges 6, cracks 12, F 15 due to checking and peeling.

LO linolenic PE alkyd: C, none.

W, excess peeling from edges, top panel removed 4, lower (approximately half of film peeled off) removed 6.

SO oleic PE alkyd: C, none.

W, excess peeling from edges, top panel removed 5; lower (few small cracks) removed 6. Panel remained very white in Weatherometer.

Varnish linseed oil: C, 2 weeks slight, increasing to heavy by 7, continuing heavy to F.

W, checking visible under magnifying glass 3; more advanced, small holes in film 8; top panel F 12 due to checking and chalking; lower F 14.

Dehydrated castor oil: C, very slight 3, very slight to slight until F.

W, very slight checking 9; slight pitting, small holes, 18–19; F 29 due to checking and C.

Commercial alkyd: C, extremely slight 3, very slight even to termination of run.

The report as published in the *Official Digest* contained graphs showing the accumulated loss in weight (in milligrams) at each reading, as a measure of erosion. It did not, however, give any indication of the original weights of the films against which to judge the severity of the losses; the manner of preparing the panels, by breaking rectangular pieces from the previously coated glass plates, precluded direct weighings. However, the panels for the Weatherometer tests were $2^5/_8 \times 6$ inches in area. For the clear vehicles a film 1.25 mils thick covering this surface would weigh approximately 306 mg. For the pigmented compounds, assuming the prescribed solvent-free thickness of 1.8 mils, the weight is calculated as approximately 930 mg.

Results were erratic; some materials lost rapidly at first, then more slowly, and others reversed this pattern. Readings extended to more than 12 weeks on only 11 of the clear and 5 of the pigmented compounds. The total accumulations for these during the number of weeks elapsed to final weighings are as follows:

Clear vehicles	Weeks	Mg. lost
Trilinolenin	22	156
PE linoleate	22	140
PE linolenate	22	180
PE linolenate (another sample)	10	252
DiPE linolenate	18	146
DiPE linolenate (another sample)	12	146
PE eleostearate	23	215
LO linoleic glycerol alkyd	18	115
SO linoleic glycerol alkyd	31	103
SO linolenic glycerol alkyd	13	90
LO oleic PE alkyd	24	75
LO linoleic PE alkyd	14	34
SO oleic PE alkyd	31	83
Pigmented Compounds		
DiPE linoleate	16	175
LO linoleic glycerol alkyd	25	183
LO eleostearic glycerol alkyd	26	139
SO linoleic glycerol alkyd	24	100
LO linoleic PE alkyd	15	127

Of the pigmented films, the alkyds (except LO linolenic PE) were superior to the esters; LO linolenic glycerol alkyd had the smallest loss of all (3 mg.) up to the time its films failed by splitting and cracking after 7 weeks. Among the oil-type paints, diPE linoleate, the two eleostearates, and dehydrated castor oil were most resistant. Among the clear films, the alkyds showed even less susceptibility to erosion than the simple esters, but for two or three of the latter the data are confusing.

Weather-Ometer Exposures of Project 17 (Chemical Changes in Films with Aging)—Northwestern Club

Project 17 was conducted by Professor R. E. Dunbar (3) with the help of his advanced students Robert J. Ludwigsen and Wesley W. Page, at the School of Chemical Technology of North Dakota Agricultural College, Fargo, North Dakota. One division of this project was a study of the chalking tendencies of the pigmented compounds when their films were exposed in the Weather-Ometer. The method was to analyze washings from the films for their content of titanium and zinc oxides.

Dr. Long had originally planned that the films, cast on glass plates, should be exposed vertically outdoors, facing south, with some device for collecting all the material that the rain washed down from each panel. At the same intervals at which these collected washings were removed and analyzed, small sections of the paint films remaining on the panels were to be scraped off and also analyzed for zinc and titanium. A balance of pigment content could presumably thus be obtained by which to follow the progress of loss of pigment from the film by disintegration at the surface. Henry A. Ball used a similar procedure in a research at Lehigh University in 1938–39. Dr. Long's outline suggested exposure in a Weather-Ometer as an alternate method; the North Dakota group adopted it, but made no analyses of film scrapings.

The intermittent water spray of the usual Weather-Ometer cycle would have washed down, with no easy possibility of recovery, some of the loosened pigment from the film surfaces. To avoid this loss, the spray was omitted. At 2-week intervals for 16 weeks, the plates as removed from the machine were cooled and washed by a jet of distilled water under a constant head for 30 seconds; these washings (about 100 ml. each) were then analyzed. Titanium dioxide was determined by a modification of Yoe and Armstrong's method (7), using a Coleman colorimeter and comparing known and unknown solutions. Zinc oxide was determined by a photometric dithizone procedure as proposed by Cowling and Miller (2).

Experimental

The samples of pigmented compounds were stored in a cool, dark place with frequent agitation until used. According to the report, the Federation drier was added in the proportion of 0.1 ml. to each gram of paint, providing a concentration of 0.025% cobalt and 0.03% lead based on total sample weight. A 3-inch Bradley blade was used in applying the films on plate glass panels $3^1/_2 \times 12 \times {}^1/_4$ inches; it was adjusted to give a dry vehicle solids thickness as close as possible to 1.25 mils. Although the plates had been cleaned only by washing with soap and water and drying with a clean towel, no crawling was experienced with any of the paints.

The amounts of pigment collected at each washing are summarized in Tables VII-7 and VII-8. Only traces of TiO_2 were yielded

TABLE VII-7
Accelerated Exposure of Pigmented Films: Milligrams of Zinc Oxide Found in Each Washing

	Weeks in Weather-Ometer							
Compound	2	4	6	8	10	12	14	16
Trilinolein	2.2	4.4	4.5	4.4	3.2	*		
Trilinolenin	1.7	2.8	3.7	4.42	3.7	*		
Trieleostearin	0.6	1.7	1.6	1.92	*			
PE oleate	1.3	2.3	1.0	1.61	2.15	2.27	*	
PE linoleate	1.4	2.2	2.4	2.53	1.5	1.51	*	
PE linolenate	None	1.3	1.8	2.17	3.41	3.78	2.1	3.69
PE eleostearate	0.2	1.0	1.3	1.27	2.14	*		
DiPE oleate	1.7	1.5	1.74	1.27	2.27	1.77	*	
DiPE linoleate	1.5	1.5	2.40	2.02	2.78	1.64	*	
DiPE linolenate	Trace	1.0	2.34	2.68	7.07	4.03	3.66	3.66
LO linoleic glycerol alkyd	None	None	None	Trace	Trace	0.88	0.88	0.88
LO linolenic glycerol alkyd	None	None	None	Trace	Trace	0.88	1.01	1.01
LO eleostearic glycerol alkyd	Trace	None	None	Trace	Trace	1.0	1.01	1.14
SO linoleic glycerol alkyd	None	None	None	Trace	Trace	0.85	Trace	Trace
SO linolenic glycerol alkyd	None	None	None	Trace	Trace	1.01	1.00	1.00
LO oleic PE alkyd	None	None	None	0.76	Trace	Trace	Trace	1.00
LO linoleic PE alkyd	None	Trace	Trace	1.05	1.26	1.28		
LO linolenic PE alkyd	None	None	Trace	Trace	1.11	1.27		
SO oleic PE alkyd	None	None	Trace	Trace	1.01	1.01		
Varnish linseed oil	1.3	2.8	2.5	3.3	2.8	*		
Dehydrated castor oil	1.3	3.0	3.8	1.8	2.1	1.64	1.83	1.89
Commercial alkyd	None	None	None	None	None	Trace	Trace	Trace

* Film too deteriorated to continue washing.

by any of the films, but all the nonalkyds lost appreciable amounts of ZnO, increasing to a peak and then falling off. A measurable amount of zinc oxide began to leach from the alkyds, in general, after 8 to 10 weeks; however, the commercial alkyd resisted leaching

TABLE VII-8

Accelerated Exposure of Pigmented Films: Milligrams of Titanium Dioxide Found in Each Washing

	Weeks in Weather-Ometer							
Compound	2	4	6	8	10	12	14	16
Trilinolein	0.05	0.05	0.2	0.02	0.02	*		
Trilinolenin	0.05	0.05	0.05	0.06	0.04	*		
Trieleostearin	None	0.05	0.05	0.02	*			
PE oleate	None	0.05	0.05	None	None	None	*	
PE linoleate	None	None	0.05	0.02	0.02	0.02	*	
PE linolenate	None	0.05	0.02	0.01	0.02	0.23	0.02	0.03
PE eleostearate	None	None	0.02	0.02	0.02	*		
DiPE oleate	None	None	0.02	Trace	0.02	0.02	*	
DiPE linoleate	None	0.05	0.02	0.02	0.02	0.02	*	
DiPE linolenate	None	0.05	0.03	0.02	0.04	0.03	0.03	0.03
LO linoleic glycerol alkyd	None	None	None	None	None	None	None	Trace
LO linolenic glycerol alkyd	None	None	None	None	None	None	None	Trace
LO eleostearic glycerol alkyd	0.05	None	None	None	None	None	None	Trace
SO linoleic glycerol alkyd	None	None	None	None	None	None	Trace	Trace
SO linolenic glycerol alkyd	None	None	None	None	None	None	Trace	Trace
LO oleic PE alkyd	None	None	None	None	None	None	Trace	Trace
LO linoleic PE alkyd	None	None	None	None	Trace	Trace	Trace	Trace
LO linolenic PE alkyd	None	None	None	None	Trace	Trace		
SO oleic PE alkyd	None	None	None	None	Trace	Trace		
Varnish linseed oil	None	0.05	0.05	0.05	0.02	*		
Dehydrated castor oil	None	0.05	0.05	0.05	None	0.02	0.02	0.02
Commercial alkyd	None	None	None	None	None	None	None	None

* Film too deteriorated to continue washing.

almost completely—only a trace was found after 12 weeks and little more after 16. Linolenic esters showed more loss than linoleic, diPE esters more than PE.

Acid and Saponification Values, Project 17—Northwestern Club

The other division of Project 17, run concurrently with the Weather-Ometer tests, was a study (3) of the effect of different conditions of light and humidity upon changes in acid and saponification values. Its purpose was to relate, if possible, these changes with the chalking and erosion characteristics of the different compounds.

For each clear and pigmented compound, with added drier, four panels were prepared, using plate glass 9 × 15 cm. (Drier was added to the pigmented compounds as described above; to the clears, at the rate of 0.1 ml. per gram of solids. The mixtures were aged 48 hours under nitrogen in a refrigerator.) The plates, with film thicknesses as nearly corresponding to 1.25 mils of vehicle solids as possible, were placed in a preliminary drying cabinet for one week. Air was circulated over a saturated solution of calcium nitrate, in a pan just below the rack holding the panels, to provide relative humidity of approximately 50%. Automatically controlled heating units and a cooling coil maintained the temperature at 77° ± 2°. A daylight fluorescent lamp, suitably masked, provided illumination of standard intensity. At the end of the week, "initial" acid and saponification values were determined and the panels were transferred to aging compartments. One panel of each clear and pigmented compound was placed in each compartment, and held under as nearly as possible the following conditions:

A. No light, 50% R.H.
B. 25 foot-candles, 50% R.H.
C. 25 foot-candles, 100% R.H.
D. Mercury arc light ("Uviarc UA-3"), 100% R.H.

Two beer coolers of the icebox type, each divided by a vertical partition, served for these compartments; they were suitably fitted with blowers, cooling coils, etc., and with pans of saturated calcium nitrate solution for the 50% R.H. condition, of saturated lead nitrate solution for 100% (water alone would have been better). A special air-cooling arrangement was rigged up to carry off the intense heat from the mercury arc lamp, which was insulated from the cabinet by UV transmitting glass. At best, however, the actual operating temperature for conditions *C* and *D* averaged 90° F.; and because the boxes could not be kept air-tight, operating humidity in that box was only 70 to 80%. In order to maintain an approximate ratio of

1:2, the humidity in the *A* and *B* compartments was allowed to drop to an average of 30 to 40%.

At 3-week intervals for 9 weeks during the aging period, and then after 6 more weeks, samples of film were scraped off with a razor blade from plates of each compound in each compartment, and duplicate determinations of acid and saponification values were made, together with blanks. For acid value, a sample of 20 to 40 mg. was refluxed for a half-hour with 10 ml. of a 1:1 mixture of 95% alcohol and benzene; after cooling, the solution was titrated with 0.01 *N* aqueous NaOH solution using phenolphthalein as indicator. For saponification value, 10 to 20 mg. of film was refluxed for 1.5 hours with 10 ml. of 0.5 *N* alcoholic KOH, cooled and titrated with 0.5 *N* HCl. Results in both cases were expressed as milligrams KOH per gram of film.

The total experimental work involved in completing the project required over 3000 separate analytical determinations—about 6000 if blanks and usual duplicates are counted. Only the most significant of the data are included in this report; saponification values were particularly erratic and fluctuating. They were apparently affected by such a variety of conditions as to be practically meaningless; however, some of the data are presented in Table XIV-28, on page 372. In some cases, duplicate determinations differed by as much as 100% of the lower value; e.g., 140.5, 65.5; 315.7, 157.5. More is involved than mere measurement of the remaining ester linkages. Carrick and associates (1) found that oxidation led to general and large increases in saponification values upon drying of tung oil; similar factors may be partially effective here.

The "initial" acid values (after 1 week of normal drying), and those after 3 weeks and 15 weeks under the four sets of aging conditions, are shown in Table VII-9 for the clear compounds and in Table VII-10 for the pigmented compounds. Acid values in general increased, especially under high humidity, except that with the alkyds, condition *C* (high humidity with daylight) produced consistently lower final values. DiPE esters seemed to yield higher acid values than PE esters.

Some yellowing in darkness was noted both with linoleic and linolenic esters, but no quantitative measurements were made.

TABLE VII-9
Changes in Acid Values of Clear Films on Aging
("Initial" and 3-week and final values for *A*, *B*, *C*, and *D* aging conditions)

		A		*B*		*C*		*D*	
Compound	Initial	3 wk.	15 wk.	3 wk.	15 wk.	3 wk.	15 wk.	3 wk.	15 wk.
Trilinolein	19.3	32.7	23.0	24.9	48.9	32.6	31.5	49.0	122.0
Trilinolenin	16.0	36.0	32.0	30.0	28.0	46.0	30.0	32.0	78.0
Trieleostearin	30.0	32.0	35.0	40.0	34.0	44.0	55.0	38.0	166.0
PE oleate	8.5	13.0	39.0	8.0	46.0	23.0	40.0	24.0	96.0
PE linoleate	83.0	24.0	31.0	40.0	33.0	28.0	45.0	53.0	130.0
PE linolenate	15.0	17.0	22.5	20.0	21.5	22.0	22.0	22.0	72.0
PE eleostearate	52.0	21.0	21.0	15.0	24.0	22.0	29.0	33.0	60.0
DiPE oleate	7.7	16.5	26.5	14.5	23.0	22.0	44.0	27.5	56.0
DiPE linoleate	17.0	24.0	27.0	24.0	27.0	29.0	51.0	58.0	158.0
DiPE linolenate	10.2	18.5	23.0	10.5	25.0	15.4	27.0	17.5	55.0
LO linoleic glyc. alkyd	21.5	17.3	18.5	12.5	19.0	9.0	14.0	13.0	35.0
LO linolenic glyc. alkyd	13.0	18.0	13.0	20.0	16.0	20.0	11.0	15.0	22.0
LO eleostearic glyc. alkyd	11.5	14.5	17.5	21.5	12.5	9.3	9.5	28.0	29.5
SO linoleic glyc. alkyd	8.0	23.0	18.0	27.0	16.5	16.0	12.0	17.0	34.0
SO linolenic glyc. alkyd	10.6	8.0	15.5	5.7	13.5	12.3	10.5	18.0	26.0
LO oleic PE alkyd	16.0	23.0	22.5	23.5	20.0	21.0	28.7	28.5	37.2
LO linoleic PE alkyd	9.5	19.0	17.4	20.5	15.8	22.5	19.0	32.0	39.3
LO linolenic PE alkyd	13.0	13.5	11.6	13.5	11.2	12.5	14.8	14.5	26.7
SO oleic PE alkyd	23.5	35.5	21.0	23.5	21.6	23.5	17.4	24.5	30.0
Varnish linseed oil	20	32.0	28.0	15.0	21.0	8.0	47.0	22.0	110.0
Dehydrated castor oil	20	11.3	23.0	7.0	28.0	11.8	43.0	15.8	72.0
Commercial alkyd	11.6	20.3	16.0	15.1	25.0	16.3	21.0	19.2	29.0

TABLE VII-10

Changes in Acid Values of Pigmented Films on Aging

("Initial" and 3-week and final values for *A*, *B*, *C*, and *D* aging conditions)

		A		*B*		*C*		*D*	
Compound	Initial	3 wk.	15 wk.	3 wk.	15 wk.	3 wk.	15 wk.	3 wk.	15 wk.
Trilinolein	30.2	28.3	25.5	26.9	26.6	27.9	24.5	24.6	26.0
Trilinolenin	27.3	17.0	11.0	16.8	17.9	19.1	17.1	15.8	18.4
Trieleostearin	13.6	10.4	9.9	14.2	13.5	13.7	11.2	12.8	18.4
PE oleate	16.5	16.0	15.6	15.1	14.1	21.4	15.2	19.3	15.3
PE linoleate	23.2	15.8	15.9	15.8	17.8	18.9	14.6	18.1	16.4
PE linolenate	12.2	11.8	9.7	14.3	15.9	11.2	12.7	10.9	12.8
PE eleostearate	13.1	11.5	10.7	12.8	12.6	10.4	12.5	15.1	13.8
DiPE oleate	12.5	17.9	12.4	15.8	10.1	19.7	11.7	15.9	13.3
DiPE linoleate	13.5	12.6	10.3	17.1	11.5	15.8	10.4	15.6	12.7
DiPE linolenate	12.6	8.2	8.8	10.8	14.2	10.1	12.6	10.3	13.9
LO linoleic glyc. alkyd	10.0	10.8	9.6	14.8	10.0	13.9	14.0	15.4	13.7
LO linolenic glyc. alkyd	8.7	10.1	7.1	9.8	7.8	10.1	12.1	8.9	12.9
LO eleostearic glyc. alkyd	11.0	13.5	6.2	12.6	8.4	12.5	11.9	15.2	10.8
SO linoleic glyc. alkyd	14.9	13.9	8.7	16.8	9.5	13.9	12.7	16.5	13.5
SO linolenic glyc. alkyd	8.7	8.1	10.8	9.7	7.7	10.1	10.9	10.6	10.8
LO oleic PE alkyd	14.4	22.3	19.2	21.8	18.6	17.7	16.9	16.1	14.0
LO linoleic PE alkyd	13.8	13.5	10.6	12.6	13.3	12.3	14.9	15.2	15.9
LO linolenic PE alkyd	13.2	12.7	10.6	10.9	13.3	9.0	14.9	10.2	13.9
SO oleic PE alkyd	16.9	19.6	10.5	18.1	12.1	21.0	—	20.3	8.9
Varnish linseed oil	27.3	20.3	18.5	19.3	18.9	17.4	22.1	20.8	21.1
Dehydrated castor oil	22.2	13.6	14.5	8.8	15.7	15.7	14.6	14.5	15.8
Commercial alkyd	22.5	24.6	21.7	52.6	20.0	49.5	21.5	14.5	20.3

Refractive Index Measurements, Project 21—Northwestern Club

Professor Dunbar's students also followed, as far as they could, the changes in refractive index of the clear compounds. These are of interest not only because high values normally accompany high diene and iodine values but also because the hiding power of a paint is proportional to the difference between the refractive index of the vehicle and that of the pigment.

Many of the usual techniques for reading the index were not applicable in following the progress of drying of these compounds. The procedure adopted (4) was that described on page 38. Films were cast on extra thin cellophane (0.00064 inch) by means of a Bradley blade, at a thickness of 1.5 mils, and small rectangular pieces were cut out at each age period and applied, film side down, against the refracting prism of an Abbé refractometer. When thicker cellophane was used readings on liquids of known index were erroneous (and variable), but with the thin grade they checked within 1 part per thousand.

Readings were made by sodium light 5, 10, 15, and 30 minutes and 1, $1^1/_2$, 2, 4, 8, 12, and 24 hours after application of films, and were continued as long as satisfactory readings could be obtained. The sharp line dividing the fields of the refractometer during early readings grew less and less distinct as oxidation and polymerization advanced; at about the tack-free point it became vague and finally disappeared.

The complete data are tabulated in Table VII-11.

It is seen that the index at first decreased with evaporation of the solvent and that thereafter the changes were fairly regular and consistent. Compounds containing eleostearic acid, which starts with conjugated unsaturation, tend to lose part of this by polymerization or oxidation and the index decreases. Trilinolenin and diPE linolenate, after initial fluctuation due to evaporation of the solvent present in the drier, showed a drop for the first 1.5 to 2 hours, then a rise for a like period, and again a drop. Trilinolein, PE linolenate, and diPE linoleate had no such temporary dip. Peroxide formation, concomitant with a shift of double bonds from unconjugated to conjugated positions, should raise the index continuously; but development of a skin, hindering access of oxygen, could account for a final decrease (6).

TABLE VII-11
Changes in Refractive Indices

Column *A:* Film age.
Column *B:* Refractive index.

Trilinolein

A	*B*
(min.)	
5	1.477
15	1.475
30	1.475
(hr.)	
1	1.476
1.5	1.479
2.5	1.479
4	1.479
6	1.483
8.5	1.489
12	1.486
24	1.486
36	1.486
72	1.493

Trilinolenin

A	*B*
(min.)	
5	1.486
15	1.486
30	1.486
(hr.)	
1	1.486
1.5	1.487
2	1.485
3	1.485
4	1.486
6	1.486

Trieleostearin

(min.)	
4	1.484
7	1.487
9	1.520
13	1.516
20	1.517
25	1.516
30	1.514

PE oleate

A	*B*
(min.)	
5	1.468
15	1.468
30	1.468
(hr.)	
2	1.468
3	1.470
6	1.469
12	1.469
25	1.470
96	1.475
168	1.478
312	1.479
672	1.479
1680	1.487

PE linoleate

A	*B*
(min.)	
5	1.477
15	1.480
30	1.481
45	1.482
(hr.)	
1	1.483
1.5	1.483
2	1.486
4	1.484
6	1.487
12	1.486
24	1.486
72	1.487

PE linolenate

A	*B*
(min.)	
2	1.485
3	1.487
5	1.485
10	1.488
15	1.488
30	1.485
(hr.)	
1	1.494
2	1.488
3.5	1.488

PE eleostearate

A	*B*
(min.)	
2	1.485
5	1.485
7	1.486
10	1.482
15	1.482
20	1.487
25	1.484
35	1.482

DiPE oleate

A	*B*
(min.)	
5	1.468
15	1.469
30	1.468
(hr.)	
1	1.469
2	1.470
3	1.470
6	1.470
12	1.470
24	1.470
48	1.473
272	1.473
216	1.480
552	1.481
1440	1.485

TABLE VII-11 (*continued*)

Column *A*: Film age.
Column *B*: Refractive index.

DiPE linoleate

A	*B*
(min.)	
2	1.477
5	1.478
10	1.478
30	1.480
(hr.)	
1.5	1.480
3	1.485
8	1.486

DiPE linolenate

A	*B*
(min.)	
5	1.489
10	1.486
30	1.486
(hr.)	
1	1.485
2	1.484
3	1.485
4	1.485

LO linoleic glycerol alkyd

A	*B*
(min.)	
2	1.470
5	1.470
7	1.473
8	1.474
11	1.476
17	1.481
30	1.488
45	1.488
(hr.)	
1	1.488
1.5	1.486
2.5	1.484

LO linolenic glycerol alkyd

A	*B*
(min.)	
1	1.470
3	1.474
6	1.484
15	1.484
30	1.486
60	1.486

LO eleostearic glycerol alkyd

A	*B*
(min.)	
2	1.470
3	1.477
5	1.478
15	1.478

SO linoleic glycerol alkyd

A	*B*
(min.)	
2	1.465
5	1.470
10	1.479
15	1.481

SO linolenic glycerol alkyd

A	*B*
(min.)	
2	1.469
5	1.480
10	1.481

LO oleic PE alkyd

A	*B*
(min.)	
2	1.462
5	1.465
10	1.467
15	1.470
33	1.482
50	1.490
(hr.)	
1.25	1.490
2.83	1.486
3.25	1.484
6	1.485
10.5	1.484

LO linoleic PE alkyd

A	*B*
(min.)	
2	1.465
4	1.464
5	1.467
10	1.478
30	1.484
(hr.)	
1	1.491
2.5	1.486
4	1.486
6	1.487

LO linolenic PE alkyd

A	*B*
(min.)	
1	1.468
3	1.470
5	1.471
10	1.475
17	1.478
30	1.486
(hr.)	
1	1.486
3	1.485

(*continued*)

TABLE VII-11 (*continued*)
Changes in Refractive Indices

Column *A:* Film age.
Column *B:* Refractive index.

SO oleic PE alkyd

A	*B*
(hr.)	
3	1.464
5	1.468
9	1.469
28	1.472
50	1.480

Varnish linseed oil

(min.)	
0	1.479
15	1.477
30	1.478
(hr.)	
1	1.478
2	1.479
4	1.483
6	1.486
8	1.490

Dehydrated castor oil

A	*B*
(min.)	
5	1.485
15	1.484
30	1.485
(hr.)	
1	1.485
3	1.489
4	1.492
6	1.492
9	1.493
11	1.495

Commercial alkyd

A	*B*
(min.)	
2	1.473
7	1.478
15	1.490
30	1.490
45	1.483
(hr.)	
1	1.484
1.25	1.483

Hardness and Abrasion Resistance, Project 22—Southern Club

Although "hardness" is a property that is difficult to define to suit all tastes, it is one that is important to makers and users of coatings. Dr. Long suggested measuring hardness with the Sward rocker or with a graduated series of pencils, and combining this measurement with a study of resistance to abrasion by falling carborundum, the Taber abraser, or other suitable method. The work was done by the team of Coulliette and Kiser at the University of Chattanooga, in connection with the erosion study of Project 13.

Portions of the same glass panels were used as for the erosion tests (page 183), since only enough of the materials could be supplied to make two drawdowns of each. Sward hardness readings were taken at several points on all panels after aging for 8 days and again after three months, and results were averaged. Some films did not dry; others were still tacky when the first measurements were made and gave zero readings.

Abrasion tests were run after aging for 1 week, except on materials that were too soft at that time. A.S.T.M. method D-968-48T was followed rather closely. A continuously rotating hopper at the top was filled with carborundum (passing 40 mesh, retained by 60 mesh) which discharged at a uniform rate of about 350 grams per minute into a glass tube 46 inches long, $^{27}/_{32}$ inch in diameter. The test panel was placed at a 45 degree angle, just below the bottom outlet of the tube. The carborundum was fed in units of 10 kg., and panel and film were weighed after being abraded by each unit. The pattern made by the falling abrasive was elliptical in shape. The end point was taken when a spot $^{5}/_{32}$ inch in diameter had worn completely through.

TABLE VII-12

Sward Hardness and Abrasion Resistance of Clear Compounds

Compound	Hardness, Sward rocker value 8 days	3 mo.	Abrasion coefficient (liters/mil)
Trilinolein	0	1	T
Trilinolenin	4	6	11.7
PE linoleate	0	3	18.9
PE linolenate	5	5	>31.5
PE eleostearate	0	2	W
LO linoleic glycerol alkyd	24	28	9.8
LO linolenic glycerol alkyd	20	24	19.2
LO eleostearic glycerol alkyd	27	30	14.9
SO linoleic glycerol alkyd	11	20	13.2
SO linolenic glycerol alkyd	4	23	17.6
LO linoleic PE alkyd	12	15	10.2
LO linolenic PE alkyd	30	30	23.4
SO oleic PE alkyd	21	25	5.4
Varnish linseed oil	0	0	T
Dehydrated castor oil	0	0	T
Commercial alkyd	10	11	11.7

Key: T, film too tacky for test; W, film wrinkled or irregular.

The panel with poorest abrasion resistance required 36 kg. of carborundum, and the best required 100 kg. The average was about 60. When the end point was reached, thickness of film was determined by a micrometer and the abrasion coefficient calculated by dividing the volume of carborundum, in liters, by the thickness, in mils. Occasionally the reproducibility was checked by testing duplicate panels (about one in five); it was always found to be within the A.S.T.M. limit of ±10%.

Tables VII-12 and VII-13 present the Sward rocker values and

TABLE VII-13

Sward Hardness and Abrasion Resistance of Pigmented Compounds

Compound	Hardness, Sward rocker value 8 days	3 mo.	Abrasion coefficient (liters/mil)
Trilinolein	6	6	11.7
Trilinolenin	5–6	6	14.2
Trieleostearin	4	6	9.4
PE linoleate	6	8	9.7
PE linolenate	6	10	12.6
PE eleostearate	4	8	11.7
DiPE linoleate	5	6	11.2
DiPE linolenate	6	10	8.9
LO linoleic glycerol alkyd	8	32	11.2
LO linolenic glycerol alkyd	3	26	—
LO eleostearic glycerol alkyd	3	6	10.6
SO linoleic glycerol alkyd	13	26	7.9
SO linolenic glycerol alkyd	4	42	14.2
LO linoleic PE alkyd	10	16	8.4
LO linolenic PE alkyd	18	28	27+
SO oleic PE alkyd	13	16	4.1
Varnish linseed oil	6	8	9.5
Dehydrated castor oil	9	10	18.0
Commercial alkyd	7	12	7.5

the abrasion coefficients for those clear and pigmented compounds on which readings could be made. Lingering tackiness (indicated by "T") made abrasion readings impossible on some; irregularity of the film, on others. The pigmented LO and SO linolenic glycerol alkyd films, though dry on top, were soft underneath, causing carborundum to stick to them, and when this sticking began, the partially abraded section of film wrinkled. After 30 days the abrasion test was repeated on these two with similar results, except that with the SO compound the sticking was not so severe and a reading was obtained. Pigmented trieleostearin lost adhesion after the film had been abraded. The clear PE linolenate stood out in abrasion resistance; its film was approximately as thick after 100 kg. had been dropped upon it as originally, and the coefficient was recorded as greater than 31.5 liters per mil. The three linolenic alkyds were also good, as was PE linoleate; other esters were poor. In general, PE oils and linolenic compounds showed superiority.

Sward rocker tests lined up in unexplainably different order from the abrasion results. After 8 days the pigmented films of LO linoleic

PE alkyd gave the highest reading, followed by SO oleic PE alkyd, SO linoleic glycerol alkyd, and LO linoleic PE alkyd. Eleostearates brought up the rear. After three months, all the pigmented compounds had hardened somewhat, especially the alkyds; SO linolenic glycerol alkyd was now the hardest, though relatively soft at 8 days. The low value for LO eleostearic glycerol alkyd might have been due to irregular film. PE and diPE linolenates were hardest among the esters and equivalent to the dehydrated castor oil control.

In the clears, the difference was much more pronounced between alkyds and esters. Again, SO linolenic glycerol alkyd was low among the alkyds after 8 days but caught up with the others in 3 months. All the oils except linolenates were too soft for a reading at the first period, and all were still relatively soft at the second. The LO oleic PE alkyd had a slight lead among the alkyds, with the commercial alkyd trailing a little behind the LO linoleic PE.

D. S. Bolley, who evaluated the data from Projects 13 and 22, assigned numerical ratings on a scale of 10 to the results of the respective series on Weatherometer behavior, hardness, and abrasion, and then combined them according to a method similar to that described in a paper on "Correlation of Evaluation Data" (5). The general scheme was to take, for each compound, selected numerical figures representing the properties studied and reduce them by division so that the maximum did not exceed a certain value, i.e., 10. These figures were then summed and averaged, giving a composite value for the compound, zero being the lowest on a scale of 10. This is of course not a statistical method for evaluation, and it contains errors due to personal opinion, differences in weighting, and selection of results. However, the various errors tend to cancel each other, and it does give a convenient method for describing data. Based on figures assigned to gloss, appearance (chalking and failure), loss in weight, hardness, and abrasion resistance, the following series of rating values was obtained.

SO linoleic glycerol alkyd	8.2
LO linoleic glycerol alkyd	7.4
Commercial alkyd	7.2
SO linolenic glycerol alkyd	6.9
SO oleic PE alkyd	6.8
LO linolenic glycerol alkyd	6.2
LO linolenic PE alkyd	6.0
LO linoleic PE alkyd	5.4

LO eleostearic glycerol alkyd	5.3
PE linolenate	4.6
Dehydrated castor oil	4.5
PE linoleate	4.0
Trilinolenin	3.8
DiPE linolenate	3.6
LO oleic PE alkyd	3.0
PE eleostearate	2.9
DiPE linoleate	2.4
Trilinolein	2.2
Varnish linseed oil	2.0
Trieleostearin	1.7
PE oleate	1.0
SO eleostearic glycerol alkyd	0.0
DiPE oleate	0.0

The two 0.0 values were due to the fact that films could not be prepared, and the poor showing of the eleostearic oils resulted from wrinkling or other defects of the film.

The alkyds show up in this table as markedly superior to the esters in this series of tests. Among the esters, linolenic compounds rank alongside the dehydrated castor oil control, followed by linoleic, eleostearic, and the linseed oil control; oleic compounds are far below. PE shows superiority to diPE, which is about equivalent to glycerol. Among the alkyds, acid ranking favors linoleic, followed by linolenic, eleostearic, and oleic. However, the estimations at best are rough, and many allowances must be made.

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CHAPTER VIII

Yellowing and Gloss

Retention of original color and luster is, of course, a desirable quality in organic coatings. But in the aging process gloss is apt to diminish, and under many circumstances yellowing of the vehicle, with consequent change of color of the paint or enamel, may become very noticeable. Some attention was paid to these changes in the course of the projects described in the two preceding chapters; a report on two other projects, devoted specifically to them, appeared in the *Official Digest,* No. 27, 280 (May, 1955).

Yellowing and Gloss, Projects 10 and 12—Philadelphia Club

R. A. Johnston and E. B. FitzGerald of the Marshall Laboratory, E. I. du Pont de Nemours & Co., Inc., Philadelphia, took charge of these two projects, which could be handled simultaneously, with only two sets of drawdowns of each clear and pigmented sample. One set was kept in the dark, the other under ordinary room illumination. The object was to compare, quantitatively, the influence of fatty acid type on color retention and luster.

Experimental

Panels used in this project were new white vitrolite glass. Drier was added to the samples in prescribed ratio, and they were aged 48 hours at 77° F. in the absence of oxygen. Films were applied by means of a blade set to give a dry thickness of 1.25 mils. Actual thicknesses measured at the end of the experiments by means of a Tukon tester were somewhat less than this, averaging 1.03 ± 0.11. Film preparation and drying for 1 week were carried out in a constant-temperature room under standard conditions. The cooperators did not receive a few of the clear samples. The clear and pigmented oleate esters did not dry, and the PE and diPE linoleates and diPE linolenate crawled, so that no data were obtained in these cases. There was not enough of any of the materials for duplicate panels in each set.

One panel of each pigmented compound was exposed under a skylight facing north in a vertical position. Under this arrangement, it was impossible to control temperature and humidity. The second set was stored in a dark room, and in order to have temperature and humidity uniform with the other set, this room was subject to the same general variations as the space under the skylight.

The clear series, done at a later time, was treated differently. All were exposed in the constant-temperature room where they had been dried. One set was placed on shelves where it received the normal room illumination; the other set was kept in a dark box.

Measurements and Calculations

Reflectance measurements from 400 to 700 mμ (i.e., the visible spectrum) were made on a General Electric recording spectrophotometer, with specular components excluded. For the clear specimens, tristimulus values were obtained by means of the G.A.F. Libroscope Tristimulus Integrator. Since this instrument was not available when the pigmented series was being run, for these panels tristimulus values were calculated by the 30 selected ordinate method described by Hardy (3).

Trichromatic coefficients were calculated from the tristimulus values and the chromaticity was then obtained as the distance in trichromatic coefficient units between the I.C.I. Illuminant C and the sample. By this procedure, values were obtained which represented only changes in chromaticity, independent of brightness. In summary, these differences in chromaticity are given by:

$$d = \sqrt{\left(\frac{X}{X+Y+Z} - X_1\right)^2 + \left(\frac{Y}{X+Y+Z} - Y_1\right)^2}$$

where X, Y, and Z are tristimulus values, $X/(X+Y+Z)$ and $Y/(X+Y+Z)$ are trichromatic coefficients, and $X_1 = 0.3101$, $Y_1 = 0.3163$ are the trichromatic coefficients of Illuminant C. Values of chromaticity calculated in this way are given as a function of panel age in Tables VIII-1 and VIII-2.

TABLE VIII-1

Yellowing and Gloss of Oil-Type Compound Films

	Pigmented				Clear		
		Distance				Distance	
Compound	Days	Light	Dark	Gloss, dark	Days	Light	Dark
Trilinolein	0	.0102	.0113	8			
	50	.0132	.0301	9			
	120	.0104	.0268	6			
	275	.0089	.0244	7			
Trilinolenin	0	.0219	.0214	63	0	.0380	.0357
	50	.0292	.0504	49	28	.0440	.0644
	120	.0192	.0527	43	75	.0657	.0907
	275	.0190	.0509	43	105	.0719	.0867
Trieleostearin	0	.0163	.0161	7			
	50	.0210	.0456	7			
	120	.0143	.0460	4			
	275	.0141	.0449	5			
PE oleate	0	Tacky	Tacky	14			
	50	.0058	.0058	14		(Crawled)	
	120	.0073	.0088	14			
	275	.0068	.0078	17			
PE linoleate	0	.0088	.0088	20	0	.0252	.0207
	50	.0128	.0250	14	28	.0350	.0509
	120	.0106	.0264	10	75	.0554	.0914
	275	.0096	.0252	11	105	.0616	.0944
PE linolenate	0	.0192	.0187	51			
	50	.0296	.0535	38			
	120	.0246	.0537	31			
	275	.0244	.0505	32			
PE eleostearate	0	.0158	.0136	6	0	.0203	.0210
	50	.0218	.0401	6	28	.0312	.0388
	120	.0171	.0406	3	75	.0500	.0664
	275	.0141	.0400	5	105	.0573	.0610
DiPE oleate	0	Tacky	Tacky				
	50	.0057	.0057	10			
	120	.0091	.0087	9			
	275	.0071	.0078	10			
DiPE linoleate	0	.0096	.0096	18			
	50	.0139	.0256	14			
	120	.0128	.0268	8			
	275	.0108	.0254	10			
Varnish linseed oil	0	.0133	.0141	23	0	.0223	.0242
	50	.0167	.0311	16	28	.0320	.0503
	120	.0126	.0321	14	75	.0520	.0952
	275	.0145	.0302	15	105	.0744	.0998
Dehydrated castor oil	0	.0063	.0069	72	0	.0128	.0127
	50	.0100	.0135	56	28	.0204	.0249
	120	.0100	.0162	56	75	.0343	.0519
	275	.0089	.0147	56	105	.0451	.0558

TABLE VIII-2
Yellowing and Gloss of Alkyd Films

	Pigmented				Clear		
		Distance		Gloss,		Distance	
Compound	Days	Light	Dark	dark	Days	Light	Dark
LO linoleic glycerol alkyd	0	.0078	.0068	69	0	.0148	.0151
	50	.0148	.0162	63	28	.0189	.0168
	120	.0137	.0180	61	75	.0228	.0219
	275	.0127	.0174	61	105	.0237	.0221
LO linolenic glycerol alkyd	0	.0091	.0093	78	0	.0165	.0164
	50	.0220	.0296	77	28	.0274	.0231
	120	.0172	.0308	77	75	.0333	.0298
	275	.0220	.0288	75	105	.0355	.0309
LO eleostearic glycerol alkyd	0	.0099	.0099	17	0	.0180	.0176
	50	.0202	.0206	14	28	.0290	.0245
	120	.0207	.0222	11	75	.0404	.0407
	275	.0204	.0224	11	105	.0430	.0431
SO linoleic glycerol alkyd	0	.0067	.0061	83	0	.0115	.0121
	50	.0132	.0135	75	28	.0157	.0155
	120	.0116	.0155	75	75	.0206	.0203
	275	.0111	.0141	76	105	.0224	.0203
SO linolenic glycerol alkyd	0	.0101	.0102	91			
	50	.0215	.0273	91			
	120	.0175	.0292	89			
	275	.0198	.0290	91			
LO oleic PE alkyd	0	—	—	—	0		.0111
	50	.0056	.0056	36	28		.0211
	120	.0067	.0079	30	75		.0205
	275	.0055	.0062	31	105		.0205
LO linoleic PE alkyd	0	.0071	.0068	61	0	.0104	.0098
	50	.0157	.0221	41	28	.0177	.0146
	120	.0118	.0232	37	75	.0259	.0227
	275	.0114	.0229	39	105	.0294	.0198
LO linolenic PE alkyd	0	.0121	.0129	93	0	.0153	.0156
	50	.0260	.0340	92	28	.0270	.0196
	120	.0191	.0362	92	75	.0358	.0244
	275	.0232	.0369	94	105	.0382	.0307
SO oleic PE alkyd	0	.0046	.0053	21	0	.0070	.0072
	50	.0095	.0081	20	28	.0121	.0107
	120	.0101	.0099	20	75	.0127	.0133
	275	.0085	.0088	21	105	.0187	.0170
Commercial alkyd	0	.0065	.0064	56	0	.0071	.0075
	50	.0123	.0136	44	28	.0104	.0102
	120	.0118	.0160	39	75	.0141	.0176
	275	.0112	.0146	39	105	.0171	.0167

In the foregoing, the tacit assumption is made that all materials changed color in the same direction, i.e., toward the same shade of yellow. The validity of this approximation may be tested by comparing the dominant wavelengths, calculated from the last reading on each panel by the graphical method of Hardy (3). The average for all panels was found to be 573.3 mμ with a standard deviation of 0.9.

Gloss values were measured in 60-degree A.S.T.M. units on the dark-exposed pigmented specimens and appear in the same tables. The panels exposed to light picked up enough dirt to interfere with dependable readings unless cleaned occasionally.

Results

The pigmented exposures were continued for 400 days and the clears for 150, but since the changes for both sets were leveling off between 50 and 100 days, only the first four readings were recorded in Tables VIII-1 and VIII-2. In several instances, small decreases in chromaticity differences can be noted at various stages in the aging period. This is particularly true of the pigmented series, subject as it was to seasonal variations in temperature and humidity.

To simplify the problem of correlation, the data were plotted and approximate slopes of yellowing vs. time curves were estimated for the first 50 days of exposure; in this region, most of the points fell on straight lines. The results of this procedure, which expresses rate of yellowing in trichromatic coefficient per day, are given in Tables VIII-3, VIII-4, and VIII-5.

If duplicate determinations could have been made, a direct estimate of the reliability of the measurements would have been possible. However, by combining error with interaction, an approximate statistical procedure can be applied to the data for the paints (Table VIII-4). It leads to the following conclusions: Yellowing of all esters and alkyds in either light or dark depends upon the nature of their acid constituent, being least with oleic and increasing through linoleic and eleostearic to linolenic. The order is the same in both light and dark, but the level of values obtained in the dark is significantly greater. Further, the degree of yellowing in the dark is directly related to oil content, i.e., greatest for pure esters, least for short-oil alkyds. In the light, this relation is not detectable.

TABLE VIII-3

Yellowing Rate of Clear Vehicle Films

(Chromaticity × 10^4/day)

Fatty acid component

Type vehicle	Oleic		Linoleic		Linolenic		Eleostearic	
	Light	Dark	Light	Dark	Light	Dark	Light	Dark
Glyceryl ester					3.7	4.7		
PE ester			4.0	9.3			4.0	6.0
LO glycerol alkyd			1.1	0.9	2.3	1.7	2.9	3.1
SO glycerol alkyd			1.2	1.1				
LO PE alkyd	1.3		2.1	1.7	2.7	1.1		
SO PE alkyd	0.7	0.8						

Varnish linseed oil		Dehydrated castor oil		Commercial alkyd	
Light	Dark	Light	Dark	Light	Dark
6.0	9.3	2.9	—	0.9	1.5

TABLE VIII-4

Yellowing Rate of Pigmented Compound Films

(Chromaticity × 10^4/day)

Fatty acid component

Type vehicle	Oleic		Linoleic		Linolenic		Eleostearic	
	Light	Dark	Light	Dark	Light	Dark	Light	Dark
Glyceryl ester			0.6	3.8	1.5	6.0	0.94	6.0
PE ester			0.8	3.2	2.0	7.0	1.2	5.3
DiPE ester			0.86	3.2				
LO glycerol alkyd			1.4	1.8	2.6	4.0	2.0	2.0
SO glycerol alkyd			1.3	1.4	2.2	3.4		
LO PE alkyd			1.7	3.0	2.8	4.2		
SO PE alkyd	1.0	0.6						

Varnish linseed oil		Dehydrated castor oil		Commercial alkyd	
Light	Dark	Light	Dark	Light	Dark
0.68	3.4	0.74	1.3	1.2	1.4

There is no discernible relationship between yellowing and alcohol type or functionality.

Incompleteness of data in the clear series hinders the analysis, but in general similar trends appear, especially with the esters and commercial vehicles. At first glance, the pure alkyds seem, peculiarly,

TABLE VIII-5
Yellowing Rate during First 50 Days
(Chromaticity × 10^4/day)

Compound	Pigmented		Clear	
	Light	Dark	Light	Dark
Trilinolein	0.6	3.8	*	*
Trilinolenin	1.5	6.0	3.7	4.7
Trieleostearin	0.94	6.0	*	*
PE linoleate	0.8	3.2	4.0	9.3
PE linolenate	2.0	7.0	*	*
PE eleostearate	1.2	5.3	4.0	6.0
DiPE linoleate	0.86	3.2	*	*
LO linoleic glycerol alkyd	1.4	1.8	1.1	0.9
LO linolenic glycerol alkyd	2.6	4.0	2.3	1.7
LO eleostearic glycerol alkyd	2.0	2.0	2.9	3.1
SO linoleic glycerol alkyd	1.3	1.4	1.2	1.1
SO linolenic glycerol alkyd	2.2	3.4	*	*
LO oleic PE alkyd	*	*	1.3	*
LO linoleic PE alkyd	1.7	3.0	2.1	1.7
LO linolenic PE alkyd	2.8	4.2	2.7	1.1
SO oleic PE alkyd	1.0	0.6	0.7	0.8

* Indicates that the sample did not dry, crawled, or was otherwise unsuited for yellowing and gloss measurements.

to have yellowed slightly more in the light than in the dark, but on closer study variability (presumably error) is seen to be greater throughout the clear data, lessening the significance of these apparent reversals. It appears safe to conclude that in tests with a larger number of clear alkyds (or with the same number done in replicate) the trend would eventually conform with that of the pigmented alkyds and all the esters and controls. The reason for greater variability in the readings on clears is easily found in the fact that the spectrophotometer light beam passes entirely through the film; thus the reflected intensity is more sensitive to thickness variations and film defects and to variations in the vitrolite.

Gloss changes appear to have no relation, in rate or extent, to structure, under the conditions of exposure in this project. However, the average level of gloss is definitely a function of the fatty acid component; it decreases from linolenic through linoleic and oleic to eleostearic. Alkyds, as expected, are higher in gloss than corresponding pure esters.

In a somewhat similar study by Hess and O'Hare (5), the finding that trilinolenin yellows more than trilinolein agrees with that of this project. However, Hess and O'Hare found more yellowing in the light than in the dark for all the materials they studied. Exposure conditions were fairly similar, but instrumentation and methods of measurement differed.

Discussion

The objective set up for Project 10 was "to correlate the rate and extent of yellowing with initial structure." Use of the word "yellowing" clearly implies that the intent was to measure a property readily observed by the eye and of practical interest to the paint industry. Reporting in terms of trichromatic coefficients does this better than recording optical densities at specified wavelengths or presenting the original spectra. For the same reason spectra were read only between 400 and 700 mμ, although a more sensitive detection and perhaps characterization of low concentrations of chromophoric groups might have accrued from extending the range down to at least 300 mμ. In spite of these limitations, there is much to learn from correlations with other projects.

Absorption spectra measured by Chipault *et al.* (Chapter XIII) in the region 221.0 to 314.0 mμ show that for most of the materials examined, diene and triene conjugations went through a maximum when an oxygen absorption of approximately 1 mole per mole of fatty acid was reached, usually in 1 to 3 days. This was followed by a decline that, judging from the curves, should have reduced such unsaturation to very low, even negligible values by the end of a week. They did not specifically look for polyenes of higher type, but these are not likely to have developed during the comparatively short aging period of their study. Although their work suggests that polyenes are readily destroyed by oxidation under the aging conditions in effect, it is still true that these structures form one of the commonest sources of yellow color in natural compounds. It is worth while to consider some of the possibilities and consequences of their formation in oxidizing drying oils.

Unsaturated acids of the type $Me(CH{:}CH)_nCOOH$ are pale yellow at $n = 3$, intense yellow at $n = 4$, and deeper in color at higher values of *n;* Hausser (4) gives absorption spectra of these.

That the formation of polymers in drying oil films may proceed according to the following sequence of reactions is suggested by Kuhn and Hoffer (6):

$$\text{—CH}_2\text{CH:CHCHO} \xrightarrow{\text{CH}_3\text{CHO}} \text{—CH}_2\text{CH:CHCH:CHCHO} + \text{H}_2\text{O} \xrightarrow[\text{Decarboxylation}]{\text{CHCOOH}_2\ +}$$

$$\text{—CH}_2\text{CH:CHCH:CHCH:CHCOOH} + \text{CO}_2 + \text{H}_2\text{O}$$

Cleavage of an initially formed hydroperoxide could have supplied the starting material; acetaldehyde has been a frequently claimed decomposition product of drying oils.

How much unsaturation of this type would be needed to account for yellowing of the intensity observed in this project, is difficult to estimate. Obviously, formation of any substantial quantity of such highly unsaturated structures would require evolution of volatile products much richer in hydrogen than the parent material; in fact, evidence for this has been claimed (2). Concurrently, the atomic ratio of hydrogen to carbon in the film should decrease, but lacking other information, we cannot take such a decrease as proof that unsaturation is being created. Removal of hydrogen atoms can be brought about either by entrance of oxygen or by formation of carbon to carbon cross-links with no change in unsaturation. In spite of these limitations it is interesting to examine the ultimate analysis given by Williams (page 81) for a typical material which yellowed strongly. Johnston and FitzGerald found (page 211) that trilinolenin reached maximum yellowness in 50 days. In the same time interval, its ultimate analysis changed as shown in Table VIII-6.

Table VIII-6. Ultimate Analysis of Trilinolenin

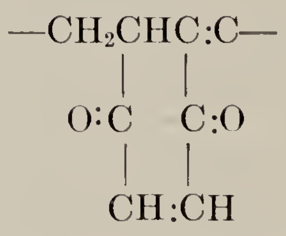
Per cent	Original (theoretical)	At 50 days
C	78.5	60.7
H	10.5	6.7
O	11.0	32.6

In other words, the composition changed from $CH_{1.61}O_{0.105}$ to $CH_{1.32}O_{0.40}$. It is clear, therefore, that although the aging film is losing hydrogen much faster than it is losing carbon in volatile products, a loss of 0.29 atom of hydrogen is counterbalanced by a gain of 0.30 atom of oxygen per atom of carbon remaining. It may be concluded that if the new oxygen enters the oil entirely as ether linkages, both the original unsaturation (0.15 double bond per C atom) and that created by dehydrogenation would be destroyed. On the other hand, if the oxygen enters in the form of carbonyl groups, then the amount of unsaturation would remain practically unchanged. It should be pointed out, however, that Williams' data contain a considerable amount of random variation, and too much emphasis should not be placed on the significance of calculations like this.

The very large increase in oxygen content shown in Williams' work suggests carbonyl structures such as the following as major sources of yellow color (1):

RCOCOR	pale yellow
RCOCH:CHCOR	bright yellow
R(CH:CH)$_2$COCOOH	bright yellow
R(CH:CH)$_3$COCOOH	orange
R(CH:CH)$_4$COCOOH	red orange

Evidence for the existence of 1,2-diketones in oxidized alkyd films has been obtained through chromatographic separation and identification by Strolle (8). In addition, spectrographic measurements led McAdie and Nicholls (page 158) to suggest the existence of quinoid structures such as



arising from cyclization of oxidized linoleates and linolenates.

Thus it could reasonably be expected that a correlation might exist between the color of oxidized films and their oxygen content, provided due allowance is made for variability of colorless ester-oxygen content of the different compounds. An approximate comparison of this sort may be made from Williams' data (pages 81–89) by calculating the net increase in oxygen content after aging. In Table VIII-7 this has been done by subtracting the theoretical initial oxygen content from the value found after aging.

Since no ultimate analyses were run on pigmented films aged in the dark, the data in the table should be compared only with the yellowing results for clear films exposed in the light. One of the most striking features of Table VIII-7 is the fact that pure esters experi-

TABLE VIII-7

Net Increase in Oxygen Content, Atoms per Mole of Compound

Material	30 days	365 days
Trilinolein	13.2	14.7
Trilinolenin	17.5	17.5
Trieleostearin	14.8	18.0
PE linoleate	14.0	21.5
PE linolenate	15.7	16.5
PE eleostearate	19.3	19.5
DiPE linoleate	22.0	26.0
DiPE linolenate	25.0	28.5
LO linoleic glycerol alkyd	7.4	18.2
LO linolenic glycerol alkyd	5.0	16.3
LO eleostearic glycerol alkyd	5.4	15.0
SO linoleic glycerol alkyd	5.0	15.6
SO linolenic glycerol alkyd	1.6	13.9
SO eleostearic glycerol alkyd	2.1	14.2
LO linoleic PE alkyd	10.7	11.3
LO linolenic PE alkyd	8.5	10.0
SO oleic PE alkyd	4.3	6.3

enced their largest increment of oxygen content in the first 30 days with only a small increase thereafter. With alkyds the reverse is true, and the increase between 30 and 365 days is, in most cases, several times as much as that at 30 days. The yellowing data, however, show that esters experienced a relatively larger change in color after 30 days than did alkyds.

Again, with one exception, oxygen increment for pure esters increases in the order linoleates, eleostearates, linolenates. But unfortunately this order is, in most cases, reversed for the alkyds. Since there is no reason to expect a totally different yellowing mechanism for alkyds, it must be concluded that no sure detailed correlation between yellowing and oxygen content can be drawn from the data. The only valid general correlation rests in the fact that pure esters yellow more than corresponding alkyds and they also undergo a larger increase in oxygen content.

The relationship between yellowing in light and in dark exposures remains to be explained. Reiney and coworkers (7) in a study of polystyrene degradation demonstrated that yellowing in dark storage was a postradiative effect, attributed to trapped radicals; however, with polystyrene, instead of being continuously progressive as in the light, it came to a stop in the dark after about 75 hours. In drying oils and alkyds, yellowing apparently continues indefinitely in the dark, even without prior exposure to light. In spite of this fundamental difference, the approach used by Reiney could undoubtedly be followed to advantage in future studies.

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CHAPTER IX

Porosity and Permeability; Water and Alkali Tests

The preservative value of paints on metals, wood, concrete, and other surfaces depends largely on their ability to keep out moisture and corrosive vapors or solutions. In view of the relative thinness of a paint coating, which must not only bar the passage of moisture but also withstand constant attack from other destructive agencies, good paints protect these surfaces remarkably well. But they are not entirely impervious to water or water vapor; hence a study of factors involved in the transmission of water, in liquid or vapor form, was an important part of the Federation project.

Dr. Long, in his outline of the program (13), said: "Any space models made for protective coating films show spaces larger than molecules of water vapor or liquid water. On a purely physical basis water molecules could, therefore, fall through these spaces and get to the surface below." This is an exaggerated concept, for molecules don't drop down holes; they obey the laws of gaseous diffusion. But it does imply the existence of pores of measurable size. H. F. Payne, who studied permeability extensively (15–19), proposed three possible mechanisms: (*a*) mass permeation through relatively large discrete pores, as in overpigmented coatings; (*b*) adsorption of water molecules on the intramolecular surfaces of polar coatings, followed by development of imbibition pressure which distends the coating and permits volume diffusion of moisture through it; (*c*) solution of water in highly polar coatings with subsequent diffusion in accordance with Fick's law. Payne made coatings which demonstrated each of these mechanisms. For normal paint coatings, mechanism (*b*) appeared to him most general. The rate of permeation by this process would be influenced by the relative polarity of the coating, the extent of cross-linking which would resist imbibition and distention, and the degree of pigmentation.

Porosity and Permeability of Films, Projects 14 and 19—Baltimore Club

This Club enlisted the services of Professor B. L. Harris, of the Department of Chemical Engineering of the Johns Hopkins University, and of some of his graduate students; it granted some of its own funds for the initial phases. Professor Harris, with Irvin Wolock, took up first the question of discrete pores, for which they developed a novel gas adsorption technique (9). In working this out on films of linseed oil, both clear and pigmented, they reached the conclusion that such pores do not exist unless the film is overpigmented. Another team compared the gas adsorption technique with other methods for determining the critical pigment concentration at which pores begin to form. With A. Bialecki, Professor Harris compared the permeabilities to water vapor of all the pure compounds of which satisfactory films could be made; for several of the alkyds, permeability to liquid water was also determined. Gas adsorption measurements were not made on the pure compounds, partly because so much time had been needed to develop the technique with linseed oil, and partly because the results with that oil had shown that pores were not likely to be found in films of the compounds.

Surface Area Measurements of Linseed Oil Films

When treated by the gas adsorption technique, porous materials exhibit a greater total surface area than do those with smooth continuous surfaces. Gas adsorption methods are ordinarily used for determining surface areas of not less than several square meters—too large to be considered with unsupported paint films. The largest practical size for these was about 1000 sq. cm. or 0.1 sq. meter. Beebe, Beckwith, and Honig (2) had developed a procedure based on that of Brunauer, Emmett, and Teller (4), using krypton gas, for surface areas of 1 sq. meter or less. It was necessary only to refine their technique to handle the small samples, but this took a bit of doing.

Two questions had first to be satisfactorily answered: whether the krypton molecule could be adsorbed in a pore which was large enough to allow appreciable permeation of water (liquid or vapor); and whether the presence of the pores in any significant quantity would increase the surface area by a measurable amount. The diameter of a krypton molecule is about 5.1 Å (2), and that of a water molecule is about 2.8 Å (3), so that a krypton molecule could enter any capillary with a diameter twice that of a water molecule. Presumably any pore large enough to allow appreciable permeation of water would have to be at least this size, for gaseous diffusion through such small pores is inappreciable and surface diffusion would probably be very low (8). On the second question, a simple calculation indicates the feasibility of surface area measurement as a criterion of the existence of pores. Take for instance a film 2 mils thick with pores 10 Å in diameter and 5000 Å (500 times their diameter) apart: the surface area is 30% greater than that of a nonporous film. The ordinary roughness of metal surfaces increases the true surface area over the geometrical area to about this same extent. If the pores are presumed to be only 500 Å (50 times their diameter) apart, increase in surface area would be 30-fold. Either of these orders of increase is readily measurable by the adsorption technique. Very large pores would escape detection by such area studies but could be determined by other methods, such as the hydrostatic procedures of Sheppard and Newsome (21), or by microscopic examination.

Surface areas were calculated from adsorption data by use of the Brunauer-Emmett-Teller equation, customarily abbreviated BET (2,4,5), as follows:

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C - 1}{V_m C} \times \frac{P}{P_0}$$

where P is the pressure of gas being adsorbed, V is the volume of gas adsorbed, P_0 is the saturation pressure of the gas at the temperature of the study, V_m is the volume equivalent to a monolayer of gas on the solid surface, and C is a constant. If $P/V(P_0 - P)$ is plotted against P/P_0, the points should lie on a straight line, in the region of P/P_0 equal to 0.05 to 0.35. The slope and intercept of this line allow evaluation of the surface area from the value of the parameter V_m, if the area of the adsorbed krypton molecule is known.

Beebe and coworkers (2) and Davis and coworkers (5) had measured the amount of krypton gas physically adsorbed by moderately small surface areas at —195° C., approximately its boiling point. However, in this study the much smaller area of the samples used made measurements at this temperature inaccurate. Lower temperatures had to be used, thus decreasing the saturation pressure and the dead volume correction. These lower temperatures were attained by maintaining the pressure of the boiling liquid nitrogen bath at a constant value below atmospheric. A bath pressure of 75 mm. Hg, corresponding to 61.9° K., was tried but was found too low; equilibrium was not reached for several hours, and small bath pressure variations caused appreciable changes in saturation pressure. These difficulties were minimized by raising the bath pressure to 235 mm., corresponding to 68.6° K. (—204.5° C.) and a liquid krypton P_0 of 0.26 mm., and this condition was established for all runs.

The published values for the area occupied by the adsorbed krypton molecule were checked by measurements on a sample of Pyrex glass spheres, first with nitrogen at 77° K., which gave an area of 4.17 meters per gram for the spheres, checking a previously determined value; then with krypton at 68° K., to show a molecular area for this gas of 21.6 sq. Å. The coefficient of expansion of glass was found to be too small in this range to make any correction necessary for the temperature difference. This molecular area agrees well with the values of 21.8 reported by Beebe *et al.* (2) on porous glass and of 21.9 and 20.4 by Davis *et al.* (5) on glass spheres, although it is higher than the *average* values of 19.5 and 20.8 for several adsorbents; the areas are known to vary with different adsorbents.

Preparation of Samples and Method of Measurement

A sample of varnish linseed oil (Spencer Kellogg & Sons' "Superior") with 0.3% lead, 0.3% cobalt, and 0.03% manganese driers (as metal) was used. The films were prepared on tinplate panels 7.5 × 8.5 cm. Each panel was first cleaned with solvent, and a strip of Scotch tape was laid across the top. The panel was coated by dipping it vertically into the oil, then raising it at the slowest constant speed of a Fisher-Payne Dip Coater. Because the oil was too fluid to cling uniformly at this speed, the film was slightly thinner at the top than at the bottom; to equalize this, panels were inverted for alternate coats. Each coat was oven-dried 24 hours at 110° C. before the next coat was applied. After the required number of coats had been applied, the Scotch tape was raised from the metal by means of a razor blade and mercury was inserted in the opening. The mercury soon worked its way between film and panel, and the stripped film could be lifted off intact. Each film had a geometric area of about

50 sq. cm.; counting both sides, a total plane surface area of about 100 sq.cm. The ten films used for a sample provided 0.1 sq. meter.

Sample films were extracted 24 hours with acetone in a Soxhlet extractor after the initial surface area determinations. The krypton adsorption was then rerun to observe the effect of extraction on the surface area.

The films were prepared of two, four, and eight coats, respectively, giving thicknesses of approximately 0.75, 1.50, and 3 mils. Single-coat films were too fragile to work with; even the thicker films tended to roll back and stick together and had to be handled with great care. It was found that the pieces of film could not be piled or rolled up for charging in the adsorption bulb; they had to be cut into small pieces and each individual piece dropped into the sample tube with minimum packing pressure. The reproducibility of independent runs on the same or similar films indicated that sticking together was practically eliminated in this way.

The first sample, the untreated eight-coat film, was placed in the bulb in a roll, and it gave a very low value for the surface area. It had been subjected to extraction before this sticking difficulty was realized; but since the values for the surface areas of the untreated two-coat and four-coat samples checked so closely, the making up of a new eight-coat sample to determine its initial area was deemed unnecessary. The "untreated" area for Sample 1 was estimated by assuming a roughness factor of 1.14—the average of those for Samples 2 and 3. The two-coat films (Sample 3) stuck together so badly after extraction that the pieces could not be separated for a gas-adsorption run.

Weight losses on extraction were determined on different films from the ones used in measuring surface area, because these picked up a small amount of mercury which, if lost during the extraction, would have introduced error.

Experimental Results

With some of the samples, krypton runs on the same sample on successive days produced BET plots which varied significantly. The samples were not removed between runs, but merely pumped overnight to evacuate the gas before the next day's run. No explanation could be found for this variation, so for better evaluation of the data, the method of least squares was applied to calculate the slopes and intercepts of all BET plots. A typical BET plot and adsorption isotherm for four-coat film, before and after extraction, are shown in Figs. IX-1 and IX-2. The experimental results on the surface area measurements are set forth in Table IX-1. The column headed "Roughness Factor" is the ratio of the total surface area, measured by krypton, to the geometrical area. For a plane surface, this value would be 1.0 if the krypton area were the true area. In general, the lower the roughness factor, the less chance for porosity. For a porosity of 30%, suggested above as a possibility, the roughness factor would be 1.3. Apparently transmission of water vapor through pores is not the only mechanism, and probably not even the main mechanism, of permeation through drying oil films.

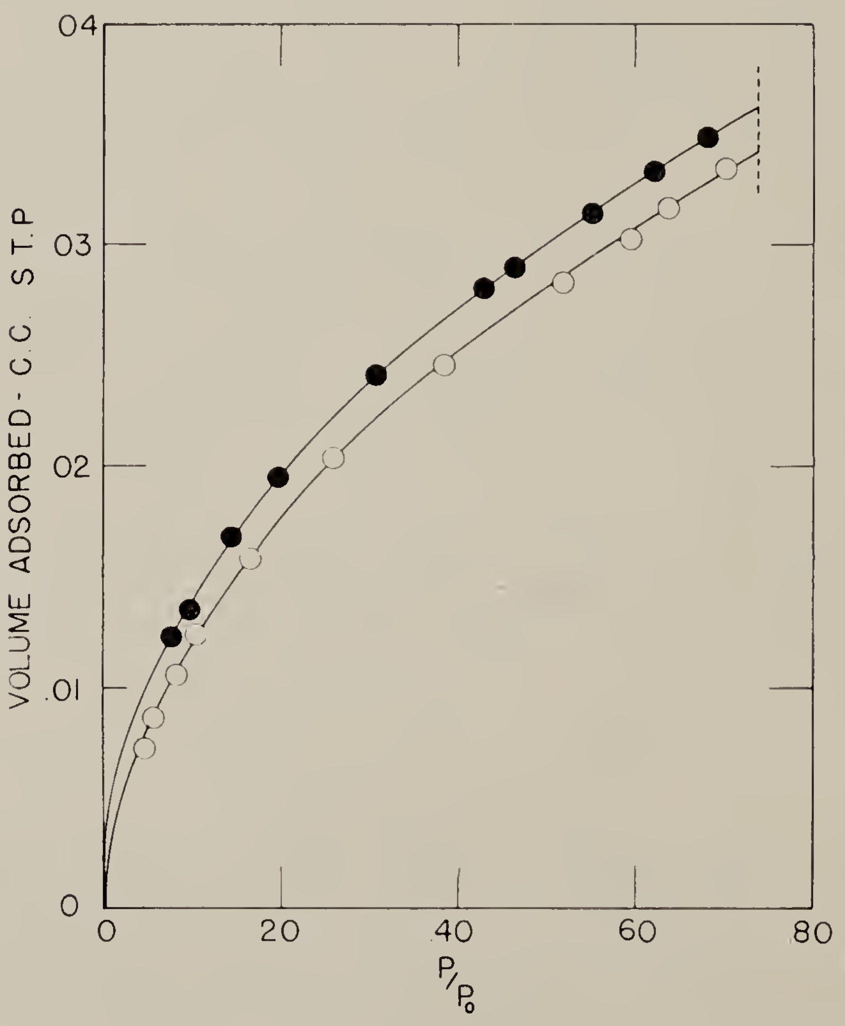

Fig. IX-1. BET plot (adsorption isotherms) of krypton on linseed oil films at 68.6° K. *Upper curve,* extracted film; *lower curve,* unextracted film.

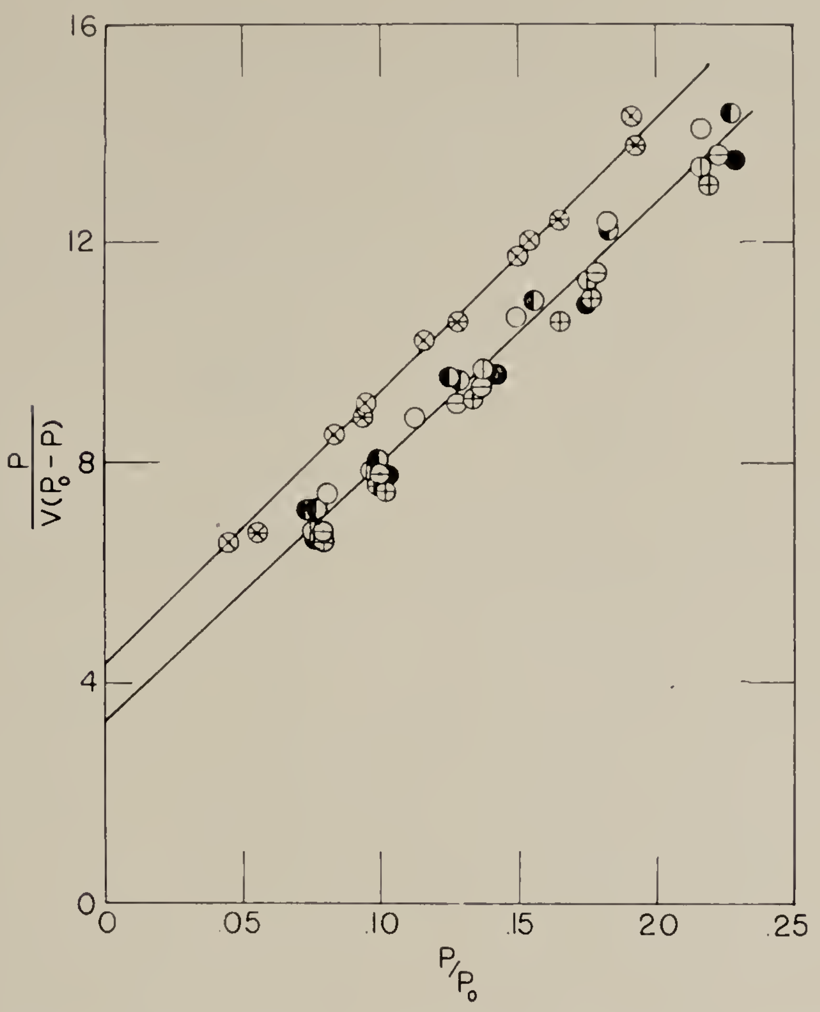

Fig. IX-2. Adsorption isotherms of krypton on linseed oil films at 68.6° K. *Upper curve,* unextracted film; *lower curve,* extracted film.

TABLE IX-1

Surface Area Measurements of Linseed Oil Films

Number of coats	Treatment	Roughness factor
2	Untreated	1.17
	Extracted 24 hr.	*
4	Untreated	1.11
	Extracted 24 hr.	1.20
	Repacked only	1.26
8	Untreated	(1.14)†
	Extracted 24 hr.	1.36
	Extracted 48 hr.	1.37

* Extracted film could not be separated for surface area determination because of sticking.

† Estimated as the average of the values for the untreated two-coat and four-coat samples; measured value too low because of faulty packing.

The weight losses on extraction appear in Table IX-2. Approximately the same total weight was lost by all three samples, with a slight increase in the roughness—so small as to rule out the possibility of creation of pores, and only a little greater for the eight-coat film, even after 48 hours extraction, than for the four-coat.

TABLE IX-2
Acetone Extraction of Linseed Oil Films

Number of coats	Initial wt. (g.)	Weight loss on extraction 24 hr.	Weight loss on extraction 48 hr.
2	0.2466	0.0366	0.0379
4	0.4124	0.0352	0.0420
8	0.8150	—	0.0453

Surface Area and Permeability Studies of Pigmented Films

The second phase of the permeability studies, as reported by Harris and Wolock (10), was suggested by work of Asbeck and Van Loo (1). These investigators had found that as the pigment volume concentration (PVC) of any given pigment-binder system is raised, there is a critical point (CPVC) at which permeability of the paint film increases markedly and other film properties undergo sharp changes. The film appears to transform from a nonporous to a porous condition owing to overpigmentation. Harris and Wolock applied the gas adsorption method to verify this assumption, using the technique described above. They checked these determinations with Payne cup permeability measurements, to make sure that their samples behaved exactly like those of Asbeck and Van Loo. The samples used were unsupported films, prepared and stripped by amalgamation in exactly the same way as those for the surface area measurements. They had been laid by a Boston-Bradley blade on tinplate panels and air-dried for 72 hours.

Of four pigment-binder systems (of which Asbeck and Van Loo kindly offered to furnish samples), the one consisting of magnesium silicate in bodied linseed oil was selected for this preliminary study. The films of this system remained more flexible at high PVC's, simplifying the preparation of specimens for both types of measurement. All samples had 0.5% lead, 0.015% manganese, and 0.015% cobalt drier (added in the form of naphthenates) as metal on the basis of vehicle solids. They contained varying amounts of bodied oil and of petroleum spirits thinner, as shown in Table IX-3, so as to step up PVC in 5% gradients from 25% to 65%. The CPVC was also determined by the Asbeck-SW CPVC cell, and the result is included in the table (data supplied by Asbeck and Van Loo).

TABLE IX-3
Composition of Magnesium Silicate–Bodied Linseed Oil Samples for Porosity and Permeability Tests: CPVC = 48%

PVC	Magnesium silicate (cc.)	Bodied oil (cc.)	Thinner (cc.)
25%	35.4	105	20
30	35.4	82.5	25
35	35.4	65.5	30
40	35.4	52.5	35
45	35.4	43.0	40
50	35.4	35.5	50
55	35.4	29.0	65
60	35.4	23.5	75
65	35.4	19.0	80

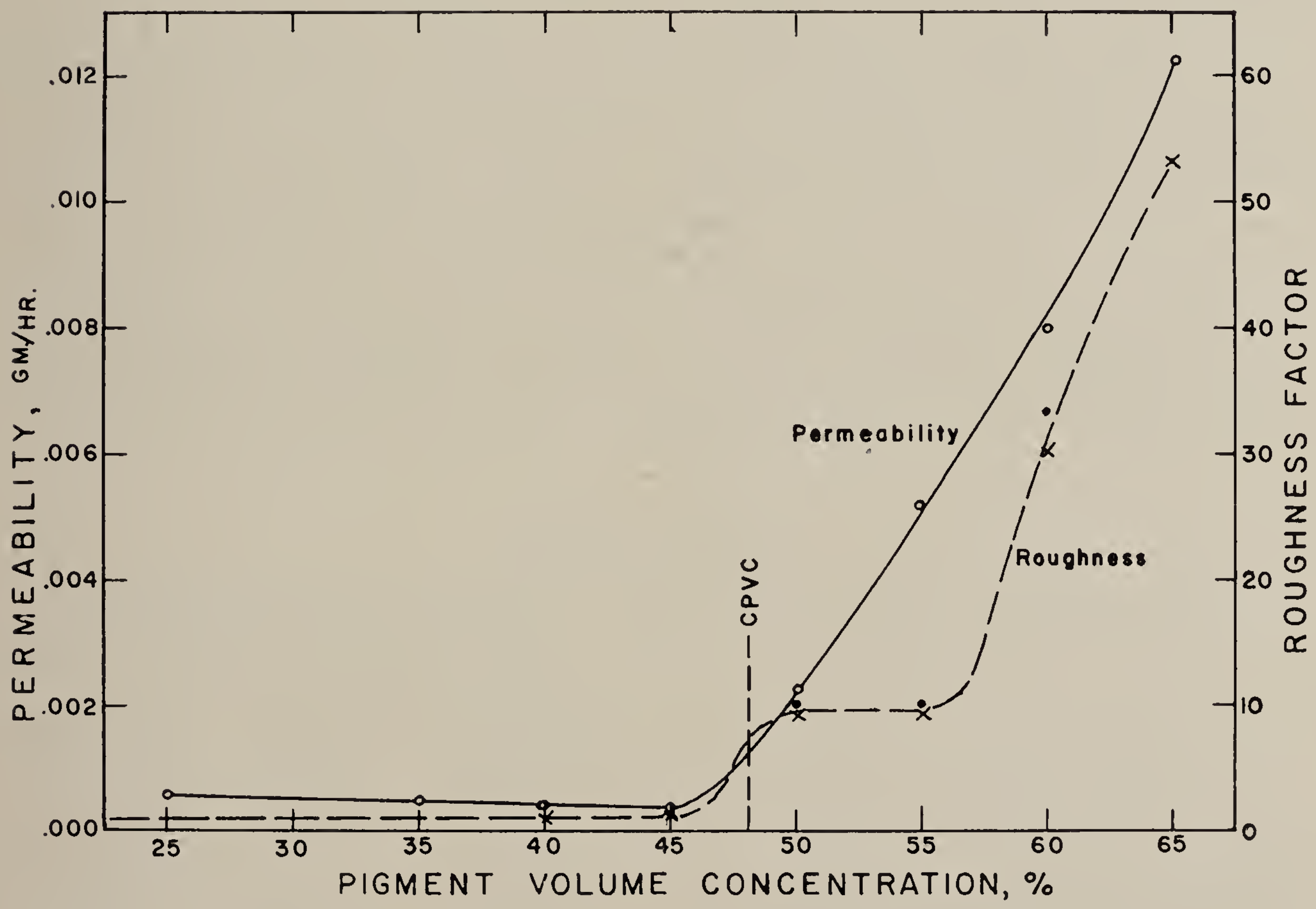

Fig. IX-3. Permeability and roughness factor of dispersions of magnesium silicate in bodied linseed oil.

Results

The Permeability-PVC curve (Fig. IX-3) roughly paralleled the curve reported by Asbeck and Van Loo (1) for the same system. Permeability decreased slightly as the PVC rose toward the critical concentration, in agreement with previous findings that pigmentation lowers permeability up to the point of overpigmentation. A sharp rise began in the region of PVC = 46% (very close to the reported CPVC) and continued with further increase of pigment.

The Roughness Factor–PVC curve in the same figure showed a value of 1.0 at 40% PVC, well below the critical value; at 45% it rose to 1.4, indicating a roughening of the surface. This was probably due to protruding pigment particles which appear as the critical concentration is approached. The Roughness Factor increased sharply in the region of the CPVC, as porosity of the film became evident in line with the permeability data. However, the leveling off of the curve just beyond this point was unexpected. It may be that at PVC = 55% there are fewer pores, but of larger diameter, thus increasing permeability but not surface area. Still higher pigmentation brought the roughness factor up steeply, indicating rapid porosity increase.

In another set of tests (6), the gas adsorption method was compared with the Asbeck-SW cell and the Payne cup as a means of determining the critical pigment volume concentration at which films become porous. Four pigment-vehicle systems were studied; titanium dioxide in raw and in bodied linseed oil, and magnesium silicate in the same two vehicles. There is such good agreement in the results (Table IX-4) that one method could be substituted for either of the others for this purpose.

TABLE IX-4

Critical Pigment Volume Concentration Determined by Various Methods

	CPVC (%) determined by		
Pigment-vehicle system	Asbeck and Van Loo cell	Permeability	Roughness factor
Titanium dioxide-raw linseed oil	33.5	34.5	34.0
Titanium dioxide-bodied linseed oil	38.5	38.5	38.0
Magnesium silicate-raw linseed oil	44.0	42.5	44.0
Magnesium silicate-bodied linseed oil	48.0	47.0	47.0

Permeability of Pure Compounds

This phase of Projects 14 and 19 was studied under Professor Harris' direction by A. Bialecki and reported in the *Official Digest,* No. 335, 884 (December, 1952). Harris and Wolock had shown that, for linseed oil films at least, there were almost certainly no discrete pores to account for permeation by water or water vapor. Solubility effects were found to have little influence; surface effects, on the contrary, had a great deal. When equilibrium was reached at a constant humidity, permeability followed Fick's law, and there was no difference between films of the same thickness whether laid in one coat or in several, if each was properly dried. This finding ruled out any possibility that the orientation of linseed oil molecules, or more complete oxidation, at the surfaces of successive coats in a multicoat system, might have an influence on the passage of vapor. Other work (20) done at Johns Hopkins led to a theory that for the mechanism of permeability the linseed oil film surface behaves as a semiliquid, and that vapor molecules approaching at high velocity strike permeation sites or "holes" in it. As soon as an equilibrium is established, permeation proceeds through these holes according to Fick's law. At higher humidities, more holes are presumably formed; permeability, in any event, increases, as was confirmed in other studies at Johns Hopkins. Edwards and Wray (7) found that after increasing fairly regularly with humidity up to 80%, permeability rose more rapidly from that point on.

Another concept of the way in which molecules enter the film and humidity affects the rate is that dipole attraction captures more molecules as vapor pressure increases, and is followed by strong adsorption at permeation sites.

Experimental

The regular series of Federation samples, and the PE esters of linseed oil acids, all with drier added as prescribed, were studied in this phase of the project. Films were drawn down on hot-dip tinplate panels, 5 × 7 × 0.01 inches, by means of a Boston-Bradley blade. Auxiliary tests showed no particular advantage in using heavier tinplate or silvered plate glass. Positioning the panels on heavy plate glass over a powerful electromagnet held them flat during the drawdown, and taping them to a flat, level table for a week or more allowed the films to dry in uniform thickness. Drying took place in a box in which standard conditions were maintained. The films were stripped by amalgamation, freed of mercury droplets by a camel's hair brush, and allowed to dry an additional 24 hours before further operations. Thickness of films was measured by surveying the panels before films were laid and after they were dry by an Ames dial gauge accurate to 0.1 ml. This procedure allowed selection of the most uniform tin panels for use, and of the most uniform portions of the films for permeability studies.

The cleaned, dried films were pressed onto aluminum gaskets and fastened onto Payne permeability cups which contained about 4 grams of anhydrous calcium chloride. They were then placed either in the box just mentioned or in desiccators at 77° F. over a saturated

TABLE IX-5

Permeability of Compounds to Water Vapor by Payne Cup Method

Compound	Average permeability constant $\times 10^7$	Average thickness (mils)	Number of samples
Trilinolein	9.4	1.09	1
Trilinolenin	0.99	1.92	2
Trieleostearin	1.12	0.28	2
PE linoleate	2.14	1.08	3
PE linolenate	0.60	1.38	2
PE eleostearate	0.52	0.27	4
DiPE oleate	16.0	2.96	1
DiPE linoleate	2.69	1.15	6
DiPE linolenate	0.75	1.36	3
LO linoleic glycerol alkyd	1.75	1.06	7
LO linolenic glycerol alkyd	0.97	1.09	5
LO eleostearic glycerol alkyd	0.96	0.99	7
SO linoleic glycerol alkyd	1.22	1.26	7
SO linolenic glycerol alkyd	0.82	0.77	3
LO oleic PE alkyd	5.26	0.89	7
LO linoleic PE alkyd	0.89	0.72	8
LO linolenic PE alkyd	0.94	0.87	7
SO oleic PE alkyd	1.46	1.14	4
PE esters of linseed fatty acids	7.00	1.60	5
Varnish linseed oil	9.2	1.62	2
Varnish linseed oil	5.43	0.53	9
Dehydrated castor oil	6.2	1.67	4
Dehydrated castor oil	2.12	0.83	6
Commercial alkyd	1.05	0.62	17

solution of calcium nitrate, providing relative humidity of 50%. Samples of which no usable films could be made were the oleate esters, which did not dry, and diPE eleostearate, which had gelled. Crawling and wrinkling made a number of the films uneven in thickness; on a few of these, poor areas were masked and correction was made for this in calculating results.

Results

The permeability constant, expressed as the number of grams of vapor transmitted, times the thickness in centimeters, divided by time in hours, area in square centimeters, and vapor pressure difference in centimeters of mercury, is shown in Table IX-5. Data on the same material varied quite widely by reason of unevenness of films or from other causes, and the figures are averages for a number of samples of the same film.

As might be expected from their oleate content, the control oils transmitted water vapor at higher rates than the pure samples. The more saturated acids imparted higher permeability, in the order oleate> linoleate> linolenate or eleostearate; there is little choice between the latter two. The glycerol esters are, in general, more permeable than those of pentaerythritol and dipentaerythritol, which are about equivalent. Higher functionality thus tends, by permitting more cross-linking, to leave the surface less "liquid-like" and to cut down the transmission. Similar trends were found in the case of the alkyds.

In comparisons of the varnish linseed oil, No. 1 of the Federation series, with other linseed oils from different sources tested in the same laboratory, good agreement was found (Table IX-6).

TABLE IX-6

Permeability of Various Linseed Oils to Water Vapor by Payne Cup Method

Oil sample	Permeability constant $\times 10^7$	Investigator
Bodied linseed oil	12	Wolock (Dissertation, Johns Hopkins University, 1951)
Bodied linseed oil	14.5	Salemi (Dissertation, Johns Hopkins University, 1952)
Bodied linseed oil	12	George (unpublished results, Johns Hopkins University)
Varnish linseed oil, No. 1	5–9	Harris and Bialecki

Permeability to Liquid Water

Transmission of liquid water through films was determined on some of the individual samples of alkyds which had been used for water-vapor studies. The only change in technique was to place liquid water inside the Payne cups, which were then inverted so that the water covered the inside of the film. The cups were placed in a desiccator, the lower compartment of which was filled with anhydrous calcium chloride, and the weight loss was recorded as a function of time.

Although this study was limited to a few samples, the data in Table IX-7 indicate roughly a permeability for liquid water only one-third of that for water vapor at 50% R.H. The general pattern is similar to that found for vapor, and the results were felt to agree reasonably well with those of other investigators.

TABLE IX-7
Permeability of Alkyd Films to Liquid Water by Payne Cup Method

Compound	Permeability constant × 10^7		Thickness (mils)
	Liquid	Vapor	
LO linoleic glycerol alkyd	0.44	1.47	1.38
LO linolenic glycerol alkyd	0.31	0.90	0.99
LO eleostearic glycerol alkyd	0.32	1.23	1.15
SO linoleic glycerol alkyd	0.42	1.28	1.04
SO linolenic glycerol alkyd	0.52	1.10	0.97
LO linoleic PE alkyd	0.94	3.09	1.06
LO linolenic PE alkyd	0.57	0.48	1.12
Commercial alkyd	0.55	1.65	1.45

General Discussion

The gas-adsorption studies show clearly that films of clear and low-pigmented coatings based on oils and alkyds do not contain discrete pores, but that films pigmented at or above the CPVC become porous and increasingly permeable. However, the precise mechanism by which moisture passes through these complex structures is still in doubt. For nonporous films, Payne and Gardner and others (16,19) found that there is an initial stage of slow permeation, but that as equilibrium is reached, under constant temperature and humidity, the rate follows Fick's law. This suggests a diffusion mechanism.

There appear to be at least two types of sorption of moisture on and in organic coatings, "chemisorption" and "volume sorption" (16,22). Chemisorption occurs on polar surfaces which provide enough points of dipole attraction to bind water molecules firmly. Chemisorption permits the development of high imbibition pressures which distend the coating structure. Volume sorption follows chemisorption on polar surfaces and establishes an equilibrium rate depending on degree of polarity, relative vapor pressures, and thickness of coating.

Chemisorption cannot develop on nonpolar surfaces; therefore the water molecules are not bound by dipole attraction and do not produce imbibition and distention of the coating. Permeation is by volume sorption only, which is necessarily quite low with nonpolar coatings. Moisture may penetrate the more or less open structures of organic coatings by a mechanism akin to capillary attraction. But moisture cannot develop sufficient imbibition pressure to permeate the structure unless the capillary surfaces are wetted. The chemisorbed moisture wets them on polar surfaces; since nonpolar surfaces have no such moisture, little or no imbibition pressure is developed and permeation is negligible.

Four chemically related materials differing in polarity illustrate this: polyethylene, poly(vinyl chloride), poly(vinyl acetate), and poly(vinyl alcohol). The rate of moisture permeation through these materials ranges from practically negligible for nonpolar polyethylene to a relatively high rate in the more polar poly(vinyl acetate); permeation is so nearly complete through highly polar poly(vinyl alcohol) that the structure disintegrates and dissolves.

Since the rate of permeation increases manyfold when films are overpigmented, it appears that beyond the critical pigment volume concentration the film contains insufficient vehicle to fill the voids between pigment particles. Moisture flows through these relatively large openings with little or no impedance and at a rate proportional to the humidity gradient across the film.

Compounds containing either more highly unsaturated acids or more polyfunctional alcohols (in either case affording a structure with more cross-linkages) have a strength or frequency of primary and secondary valence forces in the film which are harder for the permeating moisture to distend or to neutralize.

The much lower permeability found by Harris and Bialecki for liquid water was ascribed by them to adsorption of the water molecules or swelling of the film which acts to retard the permeation. This theory appears to conflict with the concept of a more open structure at higher humidities, and with the principle of thermodynamics that permeability to liquid water should be the same as for water vapor at 100% relative humidity, disregarding any surface tension or hydrostatic head effects. Sheppard and Newsome (22) mention von Schroeder's paradox, that systems in equilibrium with water vapor at 100% relative humidity will take up considerably more in liquid water. Some previous investigators have found lower permeability for liquid water than for vapor, and some have found it about the same or higher (7,12,22). The results apparently depend on the particular technique used; unknown or uncontrolled factors undoubtedly play their parts.

Water and Alkali Tests, Project 9—Cleveland Club

Since attack on films by water and by alkaline solutions is related to moisture permeability, results of the project on these tests are presented here. The work was done by George Selden and Robert C. Krueger, and a preliminary report (1950 tests) was published in the *Official Digest*, No. 322, 1042 (December, 1950). Another series of tests was run in 1951; the results are here combined.

Experimental

The A.S.T.M. procedures described in D154-47, originally contemplated for this project, were unsuitable, first because not enough material was available for coating the necessary number of panels and test tubes; second, because the compounds varied so widely in viscosity that application by pouring or dipping would have produced films of such different thicknesses that comparisons would be invalid; and third, because it was desired to report results numerically, so far as possible, rather than merely as "passed" or "failed."

Accordingly the cooperators decided to cast films of the vehicles (previously mixed with standard drier, except as noted) on picture glass panels, 8 × 10 inches, by means of a "Precision" film caster. Thickness of wet films was adjusted, with the aid of a Pfund gauge, to 1.25 ± 0.1 mils for materials of 100% solids, and to 3 mils for those containing 50% solids, the casting being repeated at a different setting where necessary. As in other projects, some films crawled, frosted, or failed to dry. The Arco Company provided an air-conditioned room in which films were dried under specified conditions for 7 days in the first series; for 7, 30, and 90 days in the second.

For the actual tests, Hellige ground glass rings 18 mm. in inside diameter, 10 mm. high were dipped in molten wax and placed in position on the test films, two rings on each film at each test period; in one was placed 1 ml. of water, in the other, 1 ml. of 3% sodium hydroxide solution. A small watch glass covered each cell.

Each sample was observed at intervals and significant changes in condition were noted. In the 1950 series of tests, records were made of water resistance after 1, 5, 24, and 48 hours; alkali after 1, 2, 5, and 24 hours. It was found that in the alkali studies, when the film failed the cell always came loose and the solution flowed out over the entire panel, ruining the film for tests at longer aging times. In the second series, therefore, observations were made more frequently. This made it possible to discontinue alkali tests after failure but before loss of adhesion of the cell, so that a given panel could serve for determinations at various ages. The more frequent readings also permitted clearer differentiation between compounds. The second series also included films of trilinolenin, PE linoleate, and diPE linoleate cast without drier. The new sample of trieleostearin used contained an antioxidant; in the first series, this compound formed a better film without than with such an additive.

The results of both series are shown in Tables IX-8 and IX-9. In reporting the first series, the cooperators assigned numerical quality ratings. In the water tests, failure at 48 hours was represented by 10; 32 hours, 8; 24 hours, 6; 5 hours, 4; failure beginning at 1 hour, complete at 5 hours, 2. Ratings in the alkali test were: 9, failed at 24 hours, OK at 5; 8, film failed at 24 hours, slightly yellow at 5; 6, film detached at 5 hours; 4, film detached at 2 hours; 2, film detached at 1 hour. A rating lower by one unit was given for films found dissolved at any immersion reading.

In Dr. R. L. Terrill's evaluation of this project, he comments that numerical quality ratings are of questionable validity for water and alkali resistance testing. For example, some of the films showed considerable immediate or early deterioration but stood up rather well on continued exposure, whereas others resisted well for some time, then failed sooner than these. Nevertheless, he assigned numeri-

TABLE IX-8
Results of Water Immersion Tests

		1 hr. exposure					3 hr. exposure		
	Compound	1950 7 day	1951 7 day	1951 30 day	1951 90 day	1951 O.N. recov. 7 day	1951 7 day	1951 30 day	1951 90 day
1	Trilinolein	cloud	lsgad	wh, lsgad	wh, lsgad	wh, lsgad	X	wh, lstad	X
2	Trilinolenin	OK	OK	sl sfg	sfg	sfg, lsgad	sfg, lsgad	soft	sfg, lsgad
3	Trilinolenin N. D.	—	sfg	sl sfg	sfg, wh	sfg, lsgad	lsgad	sfg, wh	sfg, lsgad
4	Trieleostearin	OK	lsgad	sfg, lsgad	lsgad	sfg, lsgad	dtchd	sfg, lstad	X
5	PE linoleate	OK	lsgad	sfg	wh, lsgad	wh, lsgad	dtchd	lstad	X
6	PE linoleate N.D.	—	sfg	sl sfg	sfg, wh	sfg, lsgad	dtchd	lsgad	dtchd
7	PE eleostearate	OK	lsgad	soft	lstad	sfg, lstad	dtchd	dsntd	X
8	DiPE linoleate	OK	lsgad	soft	wh, lsgad	sfg, lstad	X	sfg, lsgad	wh, lsgad
9	DiPE linoleate N.D.	—	lsgad	soft	wh, lsgad	sfg, lsgad	dtchd	sfg, lsgad	wh, lsgad
10	LO linoleic glycerol alkyd	OK	sl sfg	OK	OK sl wh	sl sfg	sl sfg	sfg, lsgad	sfg, lsgad
11	LO linolenic glycerol alkyd	OK	OK	OK	OK	sl sfg	sl sfg	sfg	OK
12	LO eleostearic glycerol alkyd	OK	OK	OK	OK	OK	sl sfg	sfg, lsgad	OK
13	SO linoleic glycerol alkyd	OK	OK	OK	OK	OK	sl sfg,	sfg, lsgad	OK
14	SO linolenic glycerol alkyd	OK	OK	OK	OK	sl sfg, wh	sl sfg, wh	lsgad	lsgad
15	LO oleic PE alkyd	*	*	wh	sfg, wh	*	*	sfg, wh	lsgad
16	LO linoleic PE alkyd	OK	OK	sfg	lsgad	sfg, lstad	X	X	X
17	SO oleic PE alkyd	OK	OK	OK	OK	OK	sfg	sfg, lsgad	OK

cal ratings to the second series, believing that such an approach was necessary for the purpose of determining possible correlations with the data of other projects.

He realized the difficulties faced in assigning proper values by anyone other than the experimental operators—difficulties mitigated in this study by the extensive notations on deterioration made by them during the tests. For a more objective method, he scored a

TABLE IX-8 (*continued*)

	5 hr. exposure				7 hr. exposure		24 hr. exposure		32 hr. exp.	48 hr. exp.
	1950 7 day	1951 7 day	1951 30 day	1951 90 day	1951 7 day	1951 30 day	1950 7 day	1951 7 day	1950 7 day	1950 7 day
1	dslvd	X	X	X	X	X	X	X	X	X
2	OK	sfg, lstad	X	sfg, lstad	X	X	lstad	X	X	X
3	—	lsgad	lstad	sfg, lsgad	X	dsntd	—	X	—	—
4	dtchd	X	X	X	X	X	X	X	X	X
5	dtchd	X	X	X	X	X	X	X	X	X
6	—	X	X	X	X	X	—	X	—	—
7	dtchd	X	X	X	X	X	X	X	X	X
8	dtchd	X	X	lstad	X	X	X	X	X	X
9	—	X	X	lstad	X	X	—	X	—	—
10	OK	sl sfg	sfg, lstad	sfg, lsgad	wh, lsgad	X	OK	X	soft	lstad
11	OK	sl sfg	sfg, lsgad	lsgad	soft, wh	fim, lstad	OK	lstad	soft	lstad
12	OK	sl sfg	X	sfg, lsgad	fim, lstad	X	OK	X	soft	lstad
13	OK	sl sfg	sfg, lsgad	sfg, lsgad	fim, lstad	fim, lstad	OK	lstad	soft	lstad
14	dtchd	sl sfg, wh	sfg, lsgad	lsgad	soft, wh	fim, lstad	X	lstad	X	X
15	*	*	X	dsntd	*	X	*	*	*	*
16	dtchd	X	X	X	X	X	X	X	X	X
17	OK	sfg, lsgad	X	fim, lsgad	X	X	lstad	X	X	X

* Not dry enough to test.

Key: dslvd, dissolved (failed); dslvg, dissolving; dsntd, disintegrated; dtchd, detached (failed); fim, film integrity maintained; lsgad, losing adhesion; lstad, lost adhesion; N.D., no drier present; OK, condition satisfactory; O.N., overnight; or, orange; sfg, softening; sl, slight; wh, whitening, hazy; wr, wrinkling; X, failed, no further test; Y, yellow; ?, questionable.

TABLE IX-9

Results of Alkali Immersion Tests

		Immediate effect		1 min. exposure			10 min. exposure		
	Compound	1951 7 day	1951 30 day	1951 7 day	1951 30 day	1951 90 day	1951 7 day	1951 30 day	1951 90 day
1	Trilinolein	sl Y	sl Y	dslvg	dslvd	dslvd	dslvd	X	X
2	Trilinolenin	Y	or	wr, dtchd	dslvd	dsntd	wr, dtchd	X	dslvd
3	Trilinolenin N.D.	or	or	dslvd	sfg, lstad	dsntd	dslvd	dslvd	dslvd
4	Trieleostearin	Y	Y	Y	sfg, lsgad	Y	dtchd, dslvg	dslvg	dsntd
5	PE linoleate	OK	Y	OK	lstad	wr, dtchd	OK	fim, lstad	dslvd
6	PE linoleate N.D.	OK	Y	OK	dslvd	dsntd	wr	X	dslvd
7	PE eleostearate	Y	Y	Y	sfg, lsgad	Y	wr	dslvg	dslvg
8	DiPE linoleate	Y	sl Y	Y	sfg, lsgad	Y, lsgad	wr, dtchd	dslvg	dsntd
9	DiPE linoleate N.D.	sl Y	sl Y	Y	lsgad	Y, lsgad	wr, dtchd	dslvd	dsntd
10	LO linoleic glycerol alkyd	OK	OK	OK	sl sfg	OK	OK	sl sfg	Y
11	LO linolenic glycerol alkyd	OK	sl Y	OK	OK	Y	OK	OK	Y
12	LO eleostearic glycerol alkyd	OK	OK	OK	sfg	Y	OK	sfg	Y
13	SO linoleic glycerol alkyd	OK	OK	OK	sfg	OK	OK	sfg	Y
14	SO linolenic glycerol alkyd	OK	Sl Y	OK	sl sfg	OK	OK	sfg	OK
15	LO oleic PE alkyd	*	(tack)	*	sfg, lsgad	dtchd	*	wh, lstad	dslvg
16	LO linoleic PE alkyd	OK	sl Y	OK	sfg, lsgad	Y	wr	sfg, lstad	dtchd
17	SO oleic PE alkyd	OK	OK	OK	sfg, lsgad	OK	OK	sfg, lstad	sfg, lsgad

given number for each notation at each period tested on the 7-, 30-, and 90-day aged films, on the following basis:

Notation	Points
None (no effect), OK	10
Slightly soft or yellow	8
Softening	7
Yellow or whitening	6
Wrinkling	5
Losing adhesion	4
Lost adhesion	2
Dissolving, disintegrating	1
Detached or dissolved	0

The points were totaled and divided by one-tenth of the highest score to obtain a "mathematical" quality rating on a basis of 10 =

TABLE IX-9 (*continued*)

	30 min. exposure			1 hr. exposure					3 hr. exposure		5 hr. exp.	24 hr. exp.
	1951 7 day	1951 30 day	1951 90 day	1950 7 day	1951 7 day	1951 30 day	1951 90 day	1951 O.N. recov. 7 day	1951 7 day	1951 30 day	1950 7 day	1950 7 day
1	X	X	X	dtchd	X	X	X	X	X	X	X	X
2	X	X	X	dtchd	X	X	X	X	X	X	X	X
3	X	X	X	—	X	X	X	X	X	X	—	—
4	X	dslvd	X	dslvd	X	X	X	X	X	X	X	X
5	dtchd	dslvd	X	dtchd	X	X	X	X	X	X	X	X
6	X	X	X	—	X	X	X	X	X	X	—	—
7	X	dslvd	dslvd	dslvd	X	X	X	X	X	X	X	X
8	X	dslvd	X	lstad	X	X	X	X	X	X	dtchd	X
9	X	X	X	—	X	X	X	X	X	X	—	—
10	OK	sl sfg	lsgad	Y	sl sfg	sl sfg	dtchd	soft	sfg, lsgad	lsgad	dtchd	X
11	OK	OK	sl sfg	Y	OK	sl sfg	dtchd	Y, sl sfg	lstad	lsgad	dtchd	X
12	OK	lsgad	sfg, lsgad	Y	OK	fim, lstad	sfg, lstad	OK	lstad	dsntd	Y	dtchd
13	OK	lsgad	lsgad	Y	OK	sfg, lstad	sfg, lsgad	sl sfg	lstad	dslvd	dtchd	X
14	OK	sfg	OK	Y	Y	sfg	sfg, lsgad	sfg, Y	lstad	sfg, lsgad	dtchd	X
15	*	dslvg	dslvd	*	*	dslvd	X	*	*	X	*	*
16	wr	sfg, lstad	dsntd	Y	wr	dslvg	X	dslvg	X	X	dslvd	X
17	wh	dslvg	dsntd	OK	wh	dslvd	X	dslvg	X	X	dtchd	X

Note: See Key to Table IX-8 on page 239.
* Not dry enough to test.

best. The results for the 1951 water immersion tests appear in Table IX-10. Agreement between these "mathematical" ratings and those assigned by comparative analysis of the data is on the whole excellent; the former tend to be lower in the lower bracket, because in comparative analysis one shuns the 0 end of the scale as indicating complete immediate failure. Since the assigned ratings were believed to correspond, in method of selection, more closely with those of the 1950 series, Dr. Terrill used these for the correlation studies. The two series show good agreement, indicating good reproducibility.

Films of the three vehicles cast without drier performed slightly better than those containing it.

TABLE IX-10

Derivation of Quality Ratings for 1951 Water Immersion Tests (and 1950 Ratings)

Compound	Points at age (days) 7	30	90	Total points	"Math." Q. R. (See Note)	"Assigned" Q. R., 1951	Q. R., 1950
Trilinolein	5	9	5	19	1.5	3	2
Trilinolenin	23	29	15	67	4	5	6
Trilinolenin N.D.	23	26	15	64	4	5	—
Trieleostearin	9	11	4	24	2	3	4
PE linoleate	9	11	1	25	2	4	4
PE linoleate N.D.	14	22	7	43	3	4	—
PE linolenate	—	—	—	—	—	—	4
PE eleostearate	7	10	2	19	1.5	3	4
DiPE linoleate	4	15	13	32	2.5	5	4
DiPE linoleate N.D.	7	15	13	35	2.5	5	—
DiPE linolenate	—	—	—	—	—	—	4
LO linoleic glyc. alkyd	49	27	27	103	7.5	7	10
LO linolenic glyc. alkyd	63	44	36	143	10	10	10
LO eleostearic glyc. alkyd	53	25	35	113	8	8	10
SO linoleic glyc. alkyd	59	36	35	130	9	8	10
SO linolenic glyc. alkyd	56	36	29	121	8.5	8	4
LO oleic PE alkyd	—	23	16	39	3	4	—
LO linoleic PE alkyd	10	10	6	26	2	3	4
LO linolenic PE alkyd	—	—	—	—	—	—	6
SO oleic PE alkyd	34	25	37	96	7	6	6
PE ester, linseed fatty acids	—	—	—	—	—	—	4
Varnish linseed oil	—	—	—	—	—	—	3
Dehydrated castor oil	—	—	—	—	—	—	4
Commercial alkyd	—	—	—	—	—	—	6

Note: So-called mathematical quality rating for 1951 series was arrived at by scoring points for immersion for various times on 7-, 30-, and 90-day-old films by assigning values from 0 to 10 for notations as described in the text. Total points were divided by one-tenth of the highest score and recorded to nearest 0.5. The assigned quality ratings were used generally in correlations, rather than the "mathematical" values.

Table IX-11 presents results similarly obtained for the 1951 alkali tests; again the "mathematical" ratings agree well with those assigned by comparative analysis and with those of the 1950 series. The largest difference (4 vs. 1) is noted in the case of PE eleostearate. Absence of drier caused poorer alkali resistance on the part of one of the three vehicles so tested.

TABLE IX-11

Derivation of Quality Ratings for 1951 Alkali Immersion Tests (and 1950 Ratings)

	Points at age (days)					"Assigned"	
Compound	7	30	90	Total points	"Math." Q. R.*	Q. R., 1951	Q. R., 1950
Trilinolein	10	8	0	18	1	2	2
Trilinolenin	10	5	2	17	1	4	2
Trilinolenin N.D.	5	7	2	14	1	4	—
Trieleostearin	15	10	8	33	2	4	1
PE linoleate	42	14	1	57	3.5	4	2
PE linoleate N. D.	27	6	2	35	2	3	—
PE linolenate	—	—	—	—	—	—	2
PE eleostearate	19	10	10	39	2.5	4	1
DiPE linoleate	16	12	4	32	2	4	6
DiPE linoleate N. D.	18	10	4	32	2	4	—
DiPE linolenate	—	—	—	—	—	—	2
LO linoleic glyc. alkyd	69	50	28	147	9	8	6
LO linolenic glyc. alkyd	72	60	32	164	10	9	6
LO eleostearic glyc. alkyd	66	38	26	130	8	7	8
SO linoleic glyc. alkyd	66	32	22	120	7.5	7	6
SO linolenic glyc. alkyd	62	45	34	141	9	9	6
LO oleic PE alkyd	0	14	2	16	1	4	—
LO linoleic PE alkyd	40	16	12	68	4	6	5
LO linolenic PE alkyd	—	—	—	—	—	—	4
SO oleic PE alkyd	50	16	16	82	5	6	6
PE ester of linseed fatty acids	—	—	—	—	—	—	1
Varnish linseed oil	—	—	—	—	—	—	1
Dehydrated castor oil	—	—	—	—	—	—	3
Commercial alkyd	—	—	—	—	—	—	9

* See Note to Table IX-10.

The 1951 series omitted some of the tests of the 1950 set, and since it was obviously desirable to have data as complete as possible for the correlation with other studies, combined quality ratings for the two sets were obtained by averaging the two values, or inserting those not duplicated. Since the ratings for 1950 and 1951 showed only one major reversal of rank order for the 46 ratings, this combination was believed justified. Table IX-12 presents results for the water and alkali tests, respectively.

TABLE IX-12

Combined Quality Ratings: 1950 and 1951 Water and Alkali Immersion Tests

	Fatty acid component							
	Oleic		Linoleic		Linolenic		Eleostearic	
Type vehicle	Water	Alkali	Water	Alkali	Water	Alkali	Water	Alkali
Glyceryl ester			2.5	2	5.5	3	3.5	2.5
PE ester			4	3	4	2	3.5	2.5
DiPE ester			4.5	5	4	2		
LO glycerol alkyd			8.5	7	10	7.5	9	7.5
SO glycerol alkyd			9	6.5	6	7.5		
LO PE alkyd	4	4	3.5	5.5	6	4		
SO PE alkyd	6	6						

Varnish linseed oil		Dehydrated castor oil		Commercial alkyd	
Water	Alkali	Water	Alkali	Water	Alkali
3	1	4	3	6	9

TABLE IX-13

Overall Combined Quality Ratings for Both Water and Alkali Tests and for Both Years (1950 and 1951)

	Fatty acid component			
Type vehicle	Oleic	Linoleic	Linolenic	Eleostearic
Glyceryl ester		2+	4+	3
PE ester		3.5	3	3
DiPE ester		5−	3	
LO glycerol alkyd		8−	9−	8+
SO glycerol alkyd		8−	7−	
LO PE alkyd	4	4.5	5	
SO PE alkyd	6			

Varnish linseed oil	Dehydrated castor oil	Commercial alkyd
2	3.5	7.5

Note: Ratings represent average of *both* water and alkali tests for both years. Order of rank is in general the same as in the water and alkali tests individually (see Table IX-12).

A further overall combined water and alkali rating for both series appears in Table IX-13. Justification for this lies in the observation that the vehicles with good water resistance also resisted alkali well; the order in rank was generally the same for the two reagents.

General Discussion

Water Resistance

The oils were inferior to the alkyds, and no significant advantage was shown by any polyalcohol. Of the glyceryl esters, linolenic was best, linoleic and eleostearic about on a par, films without drier slightly better than with. DiPE linoleate was slightly better than PE linoleate, which in turn surpassed PE eleostearate.

Among the glycerol alkyds, linolenic acid imparted slightly better resistance than linoleic; eleostearic came third. Length had little influence. Of the pentaerythritol types, the long and short oleic resins were comparable. Since the long-oil oleic resin did not dry in 7 days, tests were not run until 30 days after application; at that age and at 90 days it resisted better than its linoleic counterpart.

Alkali Resistance

As a class the oils were inferior to the alkyds; they deteriorated faster, discolored more on initial exposure.

Trieleostearin was best of the glyceryl esters, with trilinolenin and trilinolein following. Drier made no appreciable difference. PE and diPE linoleates were comparable; PE eleostearate was slightly better than PE linoleate.

For the glycerol alkyds, no significant difference appeared between short and long linoleic and linolenic resins. Linolenic was best of the acids, followed by linoleic and eleostearic, which were comparable but slightly inferior. The short and long oleic PE alkyds were close in alkali resistance; the long oleic resin, though not dry enough for the 7-day tests, matched the LO linoleic PE alkyd thereafter.

In general, poorer results for both water and alkali resistance are found with increasing film age, although no quantitative interpretation is possible. There are anomalies in both the 1950 and 1951 series; the relative agreement between them points toward properties inherent in the compounds themselves as being responsible. Before the hydroxyl values of the compounds had been determined (after these tests had been completed), it was thought possible that free hydroxyl groups, as vulnerable points of attack, might prove to offer a partial explanation. But these values, when at hand, did nothing to bring the unexpected results into line with practical experience. In comparing the three linolenate esters, for example, trilinolenin with better overall performance has the highest hydroxyl value. And in comparing the PE esters of the three acids, the eleostearic ester has the highest hydroxyl value, but it hardly seems high enough (particularly in comparison with that of trilinolenin) to be of significant effect. The relatively poor showing of the eleostearate compounds in general is probably due to the fact that they were not gas-proof.

Compound	Combined water rating	Combined alkali rating	Hydroxyl value
Trilinolenin	5.5	3	17.2
PE linolenate	4	2	6.3
DiPE linolenate	4	2	6.8
PE linoleate	4	3	2.0
PE linolenate	4	2	6.3
PE eleostearate	3.5	2.5	13.9

The alkyds which in general received highest ratings were also the compounds generally showing the highest hydroxyl numbers; a reverse correlation very nearly exists. The occasional unreliability of hydroxyl content as a measure of performance, pointed out in previous publications (11), seems to be borne out in this study.

Rangers of hydroxyl values between 50 and 80 for short-oil alkyds and between 25 and 50 for long-oil alkyds have been stated (14) to be reasonably satisfactory compromises with minimum effects on properties. The Federation compounds fall near or within this range; however, the long-oil PE alkyds have hydroxyl numbers *below* 25 but are nevertheless outperformed by their glycerol counterparts. Thus even within the resin series hydroxyl values have no relation to water and alkali resistance.

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CHAPTER X

Oxygen Penetration and Shrinkage of Films

Chapter IV stated that at the point when a film sets to touch, or in other words when the surface of the film changes from liquid to solid, the rate of absorption of oxygen drops sharply but does not usually fall to zero. The frequent observation that films quite hard on top are soft underneath prompted the inclusion in the program of a study (Project 18) of the depth to which oxygen penetrates paint films of varying thicknesses. Dr. Long proposed that samples of the pure compounds, possibly as much as an inch deep, be exposed in small vessels for a given period, then frozen in liquid nitrogen. Horizontal slices about 2 mils thick were to be cut with a microtome at various distances up to about 0.1 inch below the surface. Ultimate analyses of these slices for carbon and hydrogen (and oxygen by difference) would show how far oxygen had worked into the film.

Another project, No. 20, was concerned with the change in volume that a film undergoes in transforming from liquid to solid, and with the effect on this of the degree of unsaturation of the fatty acids involved. A comparison was proposed, but was not attempted, between the final volumes of films dried while adhering to a surface and those dried without restraint, as while floating on mercury.

Oxygen Penetration, Project 18—University of Michigan

Professor L. L. Carrick, of the Department of Chemical and Metallurgical Engineering of the University of Michigan, supervised the work on these projects done by W. J. Snoddon and A. J. Permoda, respectively, under Federation fellowships. Reports appeared in the *Official Digest*, No. 322, 682–700 (November, 1951). However, in the report by Carrick and Snoddon on Depth of Oxygen Penetration, the PE and diPE linolenates were incorrectly referred to as linoleates.

Since the proposed outline for the oxygen-penetration project entailed a large volume of analytical work, it was decided to limit the number of vehicles to six: varnish linseed oil, trilinolein, trilinolenin, trieleostearin, and PE and diPE linolenates. (For Project 20, dehydrated castor oil of Z-3 viscosity was added to this list.)

Experimental

To each material, as it was removed from its sealed ampule, Federation drier was added in the prescribed proportion, and the sample was evacuated at an absolute pressure of 6 mm. of mercury under a bell jar for several hours until solids reached 98% or more. Oxygen-free nitrogen was then admitted to the jar and the sample capped. It was aged at least 24 hours under nitrogen.

For each material, films of two thicknesses (1.1 to 1.6 and 2.7 to 4.3 mils, depending on viscosity) were applied on glass plates which had been cleaned with alcohol, by means of a mechanically driven applicator loaned by Titanium Division of National Lead Co. In addition, two thicker films, approximately 10 and 25 mils each, were formed on glass plates which had strips of glass cemented to them at the edges (Fig. X-1) to prevent flow. The films were dried under the prescribed conditions, and samples were cut by razor blade from each film after 1, 2, 7, and 30 days. Carbon and hydrogen were determined in Fisher Scientific Company's Micro Carbon and Hydrogen Apparatus by procedures following in general those of Niederl and Niederl (3).

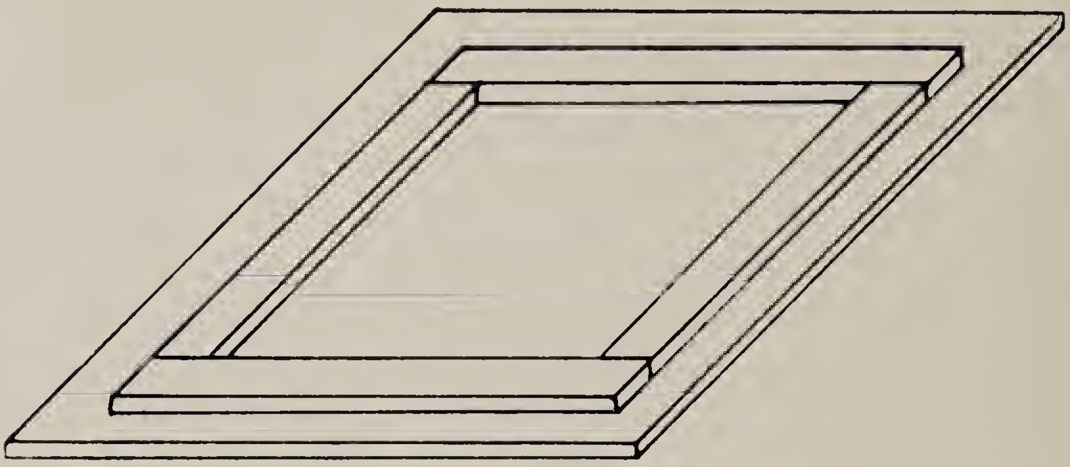

Fig. X-1. Glass panel used for films of 10- and 25-mil wet thicknesses.

All the thicker films wrinkled badly; the 25.2-mil trieleostearin film was the worst, the corresponding one of diPE linolenate the best, of that series (Fig. X-2). After 30 days, a portion of this last film of 18 mils dry thickness was sliced into three horizontal segments of approximately 6 mils each. In addition to the usual analyses on this compound, the oxygen content of each segment was determined.

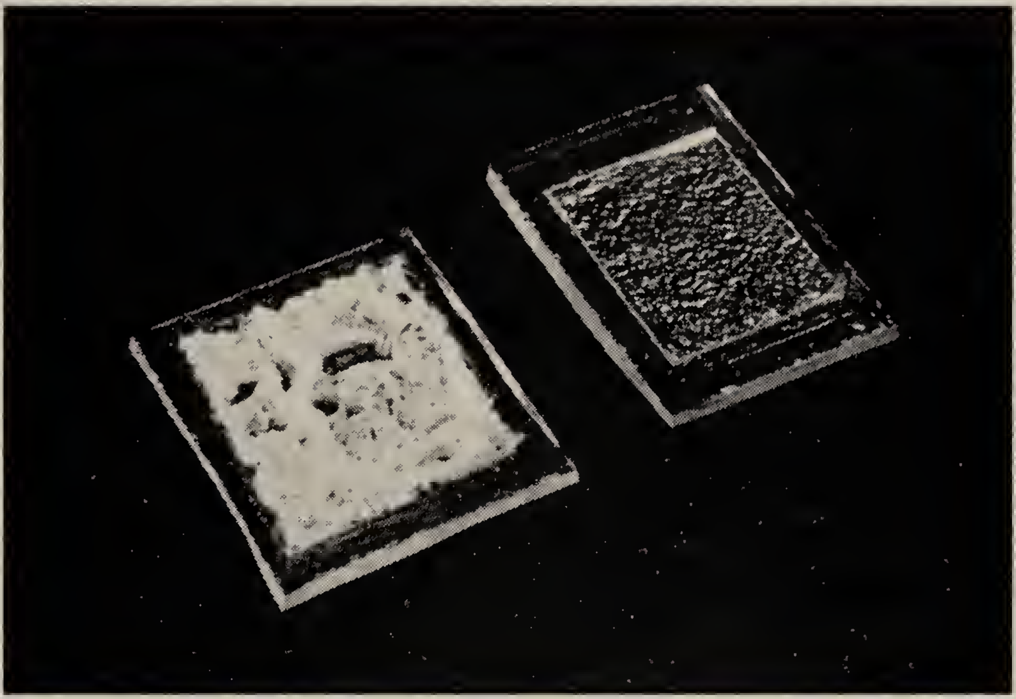

Fig. X-2. Dried films of trieleostearin (*left*) and diPE linolenate (*right*); wet thickness about 25 mils.

Results

These are tabulated in Tables X-1 to X-7 and plotted in Figs. X-3 to X-8. As was found by Williams (Chapter IV), the thinner films generally attained their maximum oxygen content after 1 day. Linseed oil, with its usual induction period, took 2 days. The figure for oxygen was about equal to that calculated assuming one oxygen molecule associated with each double bond in the molecule of the compound. On succeeding days, oxygen content declined slightly, then remained approximately constant. This behavior was explained by assuming that at the maximum point, when the films were still mostly liquid, volatile decomposition products were emitted in sufficient amount to reduce the net oxygen content; but as the films solidified, reduced activity of the larger molecules in forming volatile products, and increased resistance to gaseous diffusion, prevented much further change.

For the thicker films such a maximum was not observed, probably owing to the larger volume of vehicle for the same surface area and

TABLE X-1

Carbon, Hydrogen, and Oxygen Content of Trilinolein Films

(Sample at start: 77.7, 77.8% carbon; 11.2, 11.3% hydrogen; 11.1, 10.9% oxygen)

Exposure period		Wet film thickness			
		1.4 mils	2.7 mils	10.1 mils	25.7 mils
1 day	%C	61.5	63.1, 62.2	68.8, 69.4	71.9, 72.5
	H	8.9	9.1, 10.7	9.1, 10.6	9.1, 10.7
	O	29.6	27.8, 27.1	22.1, 20.0	19.0, 16.8
2 days	%C	62.5, 63.5	65.4, 64.4	67 5, 68.2	69.2, 69.7
	H	8.7, 9.0	9.4, 8.9	9.8, 9.5	10.2, 9.9
	O	28.8, 27.5	25.2, 26.7	22.7, 22.3	20.6, 20.4
7 days	%C	61.9, 60.0, 63.8	63.8, 62.8	64.9, 65.9	68.1, 67.2
	H	9.1, 8.5, 9.6	8.9, 8.9	8.8, 9.2	9.7, 9.2
	O	29.0, 30.9, 26.6	27.3, 28.3	26.3, 24.9	22.2, 23.6
20 days	%C			65.6	
	H			9.7	
	O			24.7	
30 days	%C	61.8, 60.9	62.2, 62.1	65.8	68.3, 66.7
	H	9.0, 8.3	8.6, 8.7	9.3	9.6, 9.2
	O	29.2, 30.8	29.2, 29.2	24.9	22.1, 24.1

TABLE X-2

Carbon, Hydrogen, and Oxygen Content of Trilinolenin Films

(Sample at start: 77.2, 77.7% carbon; 10.9, 11.1% hydrogen; 11.9, 11.2% oxygen)

Exposure period		Wet film thickness			
		1.2 mils	3.4 mils	10.4 mils	26.9 mils
1 day	%C	60.3, 57.9	65.1, 68.3	70.8, 72.1	70.9, 70.3
	H	7.6, 8.6	8.9 8.7	10.0, 9.7	10.0, 9.3
	O	32.1, 33.5	26.0, 23.0	19.2, 18.2	19.1, 20.4
2 days	%C	60.7, 61.8	67.1, 66.7	68.0, 69.2	70.3, 69.5
	H	8.6, 8.0	8.3, 9.3	9.8, 9.8	10.5, 9.5
	O	30.7, 30.2	24.6, 24.0	22.2, 21.0	19.2, 21.0
7 days	%C	58.5	66.7, 66.8	68.6, 67.2	68.8, 70.4
	H	8.9	9.3, 8.9	9.2, 9.4	9.5, 9.4
	O	32.6	24.0, 24.3	22.2, 23.4	21.7, 20.2
30 days	%C	62.8, 60.3	62.9, 63.2	66.1, 66.3	65.9, 67.7
	H	8.4, 8.4	8.8, 8.4	8.5, 8.6	9.8, 9.4
	O	28.8, 31.3	28.3, 28.4	25.4, 24.1	24.3, 22.9

TABLE X-3

Carbon, Hydrogen, and Oxygen Content of Trieleostearin Films

(Sample at start: 79.1, 78.1% carbon; 10.8, 10.6% hydrogen; 10.1, 11.3% oxygen)

Exposure period		Wet film thickness			
		1.6 mils	3 1 mils	13.6 mils	25.2 mils
1 day	%C	61.9, 63.1	65.9, 67.5	72.2, 72.8	73.8, 73.8
	H	8.4, 8.5	8.5, 9.1	9.9, 9.9	10.4, 9.9
	O	29.7, 28.4	25.6, 23.4	17.9, 17.3	15.8, 16.3
2 days	%C	62.0, 63.3	63.6, 64.0	67.3, 67.8	69.5, 71.5
	H	9.1, 8.5	8.6, 8.4	9.5, 9.2	9.6, 9.5
	O	28.9, 28.2	27.8, 27.6	23.2, 23.0	20.9, 19.0
7 days	%C	62.7, 62.0	62.7, 62.3	64.1, 62.9	68.1, 68.4
	H	8.0, 8.1	8.3, 8.9	9.6, 8.6	9.5, 8.3
	O	29.3, 29.9	29.0, 28.8	26.3, 28.5	22.4, 22.3
30 days	%C	60.8, 61.8	61.3	62.0, 61.6	64.6, 62.8
	H	8.0, 8.4	8.3	8.8, 8.2	8.5, 8.6
	O	31.2, 29.8	30.4	29.2, 30.2	26.9, 28.6
7 days	%C	61.2*, 62.4*			
	H	8.1*, 6.8*			
	O	30.7*, 30.8*			

* Film 1.4 mils thick.

TABLE X-4

Carbon, Hydrogen, and Oxygen Content of PE Linolenate Films

(Sample at start: 76.7, 77.3% carbon, 10.8, 10.6% hydrogen, 12.5, 12.1% oxygen)

Exposure period		Wet film thickness			
		1.4 mils	4.3 mils	10.5 mils	25.1 mils
1 day	%C	61.0, 63.2	66.2, 67.6	67.7, 67.6	71.8, 71.4
	H	9.0, 8.7	9.0, 8.9	8.8, 9.0	9.8, 9.4
	O	30.0, 28.1	24.8, 23.5	23.5, 23.4	18.4, 19.2
2 days	%C	62.6	68.0, 68.5	69.2, 70.8	70.5, 72.9
	H	8.8	9.5, 8.9	9.4, 9.2	9.5, 9.1
	O	28.6	22.5, 22.6	21.4, 20.0	20.0, 18.0
7 days	%C	62.8, 64.2, 63.5*	67.7, 67.5	68.7, 68.2	70.5, 69.9
	H	8.8, 8.9, 8.8*	9.0, 9.5	9.4, 9.1	9.4, 9.4
	O	28.4, 26.9, 27.7*	23.3, 23.0	21.9, 22.7	20.1, 20.7
30 days	%C	64.5, 63.8	65.9, 65.5	69.0, 68.9	70.3, 69.0
	H	8.8, 8.6	9.1, 8.6	9.6, 9.6	9.6, 9.4
	O	26.7, 27.6	25.0, 25.9	21.4, 21.5	20.1, 21.6

* Film 1.1 mils thick.

TABLE X-5

Carbon, Hydrogen, and Oxygen Content of DiPE Linolenate Films
(Sample at start: 76.3, 76.7% carbon, 10.3, 10.6% hydrogen, 13.4, 12.7% oxygen)

Exposure period		Wet film thickness			
		1.1 mils	3.9 mils	10.1 mils	24.9 mils
1 day	%C	62.6, 63.2	68.5, 69.3	67.8, 69.4	71.1, 71.6
	H	9.0, 8.4	8.7, 9.5	9.5, 9.3	9.4, 9.8
	O	28.4, 28.4	22.8, 21.2	22.7, 21.3	19.5, 18.6
2 days	%C	64.2, 63.4	68.0, 69.0	69.9, 68.4	70.6, 71.9
	H	8.8, 9.0	9.2, 9.7	9.1, 9.4	9.7, 9.7
	O	27.0, 27.6	22.8, 21.3	21.0, 22.2	19.7, 18.4
7 days	%C	63.3, 63.9*	67.7	69.3, 68.4	70.6, 71.9
	H	9.1, 8.5*	9.3	9.3, 9.2	9.2, 9.6
	O	27.6, 27.6*	23.0	21.4, 22.4	20.2, 18.5
30 days	%C	61.5	67.3, 68.7	67.2, 67.3	69.3, 70.7
	H	9.0	8.1, 9.0	10.2, 9.5	9.0, 9.6
	O	29.5	24.6, 22.3	22.6, 23.2	21.7, 19.7

* Film 1.5 mil thick.

TABLE X-6

Carbon, Hydrogen, and Oxygen Content of Horizontal Segments of DiPE Linolenate Film (Wet Thickness 25 Mils, Dry Thickness 18 Mils)

Film segment	Analyses at 30-day period	
Surface to 6 mils below depth	%C	69.8, 69.2
	H	9.9, 9.5
	O	20.3, 21.3
6 to 12 mils	%C	71.1, 72.2
	H	10.3, 10.1
	O	18.6, 17.7
12 to 18 mils	%C	71.7, 73.2
	H	10.9, 9.8
	O	17.4, 17.0

the greater mean distance of gaseous diffusion. Oxygen uptake fell off or even stopped, at a much lower content of this element than for thin films. The curves for trilinolein and the PE and diPE linolenates had almost leveled off at 30 days, but trilinolenin and trieleostearin were still gaining.

The excessive wrinkling of the thicker films made it practically impossible, except in the one case, to determine oxygen content as a

TABLE X-7

Carbon, Hydrogen, and Oxygen Content of Varnish Linseed Oil Films

(Sample at start: 79.5, 78.9% carbon, 9.0, 9.4% hydrogen, 11.5, 11.7% oxygen)

Exposure period		Wet film thickness			
		1.4 mils	4.3 mils	10.0 mils	25.7 mils
1 day	%C	67.5, 65.5*, 67.3†, 67.4†	67.0, 68.5	73.6, 71.1	73.9‡, 72.5‡
	H	9.7, 9.7*, 9.8†, 10.0†	9.7, 9.5	10.3, 9.6	10.6‡, 10.4‡
	O	22.8, 24.8*, 22.9†, 22.6†	23.3, 22.0	16.1, 19.3	15.5‡, 17.1‡
2 days	%C	63.2	65.7, 67.4	70.1, 70.7	70.8, 71.2
	H	9.3	9.7, 9.5	10.1, 9.9	10.3, 10.3
	O	27.5	24.6, 23.1	19.8, 19.4	18.9, 18.5
8 days	%C	63.4, 64.0	67.1, 65.6	68.1, 68.5	70.0, 70.0
	H	9.5, 9.4	9.1, 9.1	9.6, 9.1	9.9, 9.6
	O	27.1, 26.6	23.8, 25.3	22.3, 22.4	20.1, 20.4
30 days	%C	63.6, 63.8	64.6, 64.6	66.3, 67.3	68.5, 69.6
	H	9.4, 9.0	8.9, 8.7	9.8, 9.7	10.1, 9.7
	O	27.0, 27.2	26.5, 26.7	23.9, 23.0	21.4, 20.7
60 days	%C		63.2, 63.8		
	H		8.9, 9.0		
	O		27.9, 27.2		

* Film 1.0 mil thick.

† Film 2.1 mils thick.

‡ Film 27 mils thick.

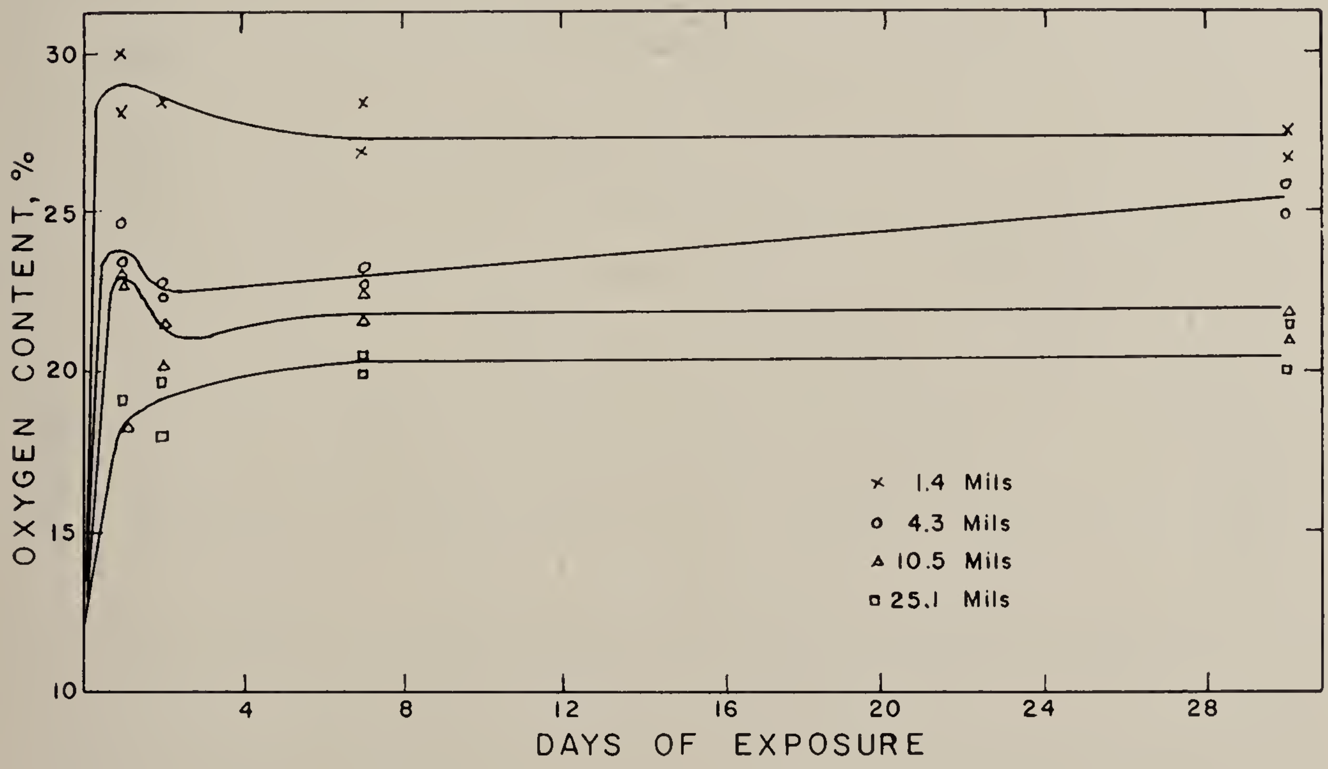

Fig. X-3. Oxygen content of trilinolein films of graduated thicknesses.

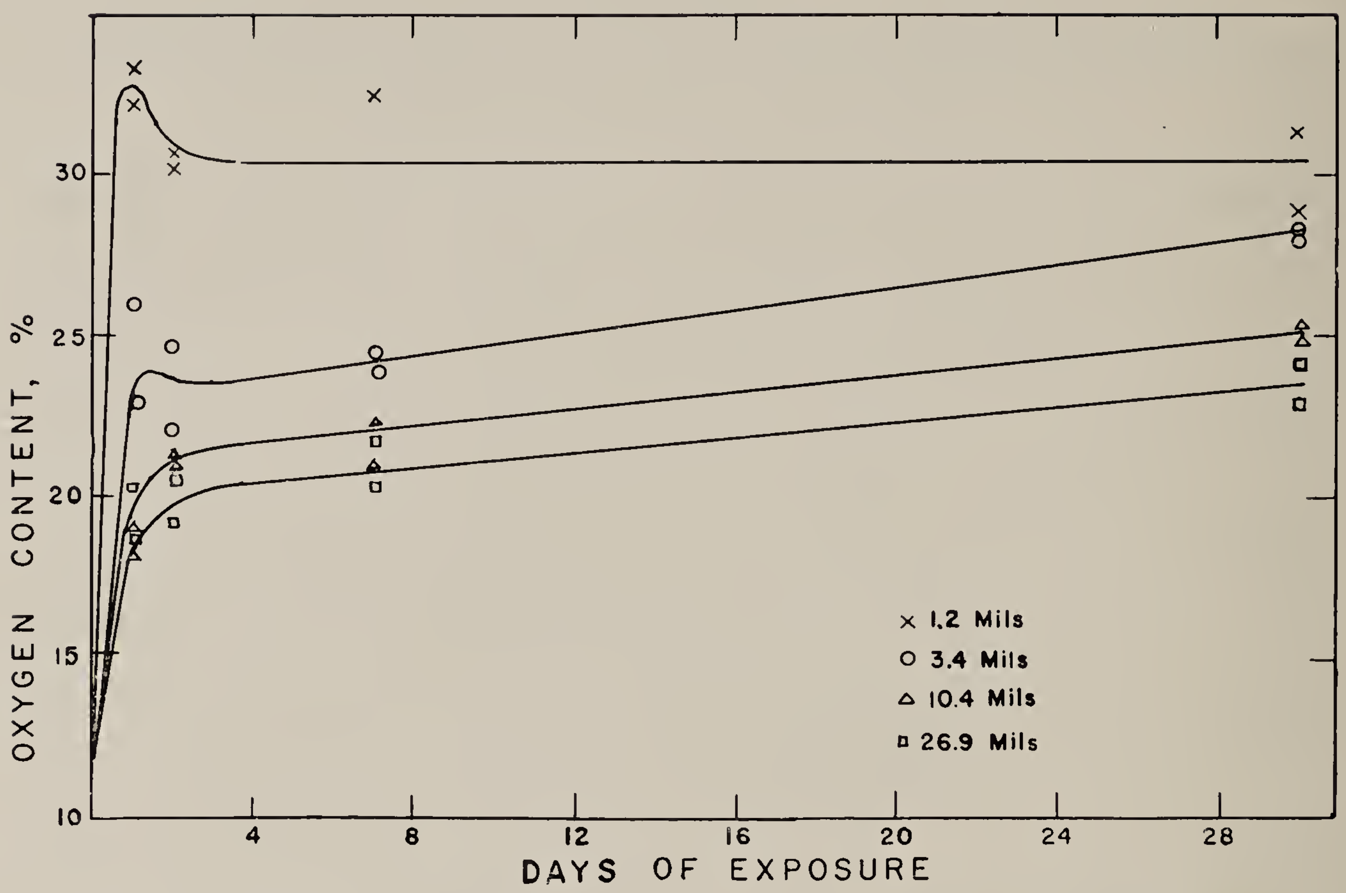

Fig. X-4. Oxygen content of trilinolenin films of graduated thicknesses.

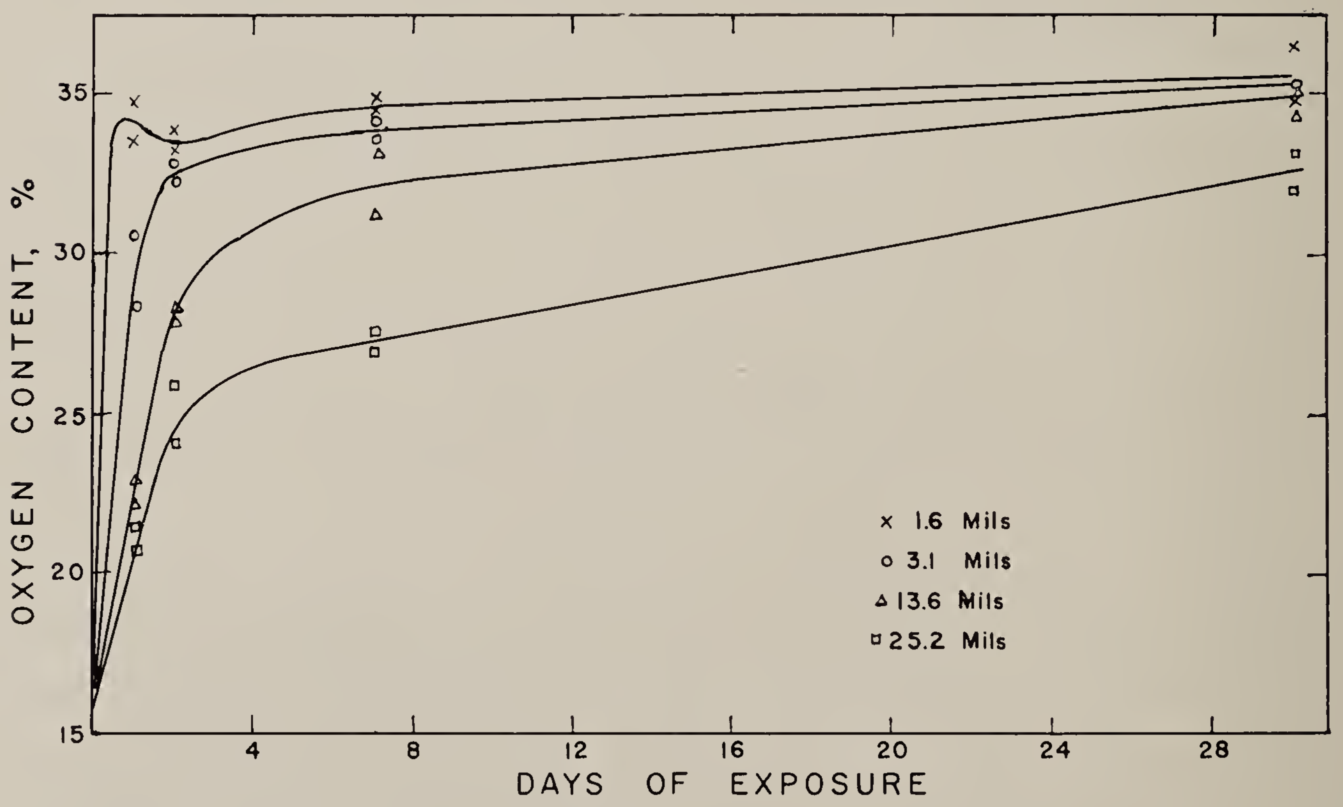

Fig. X-5. Oxygen content of trieleostearin films of graduated thicknesses.

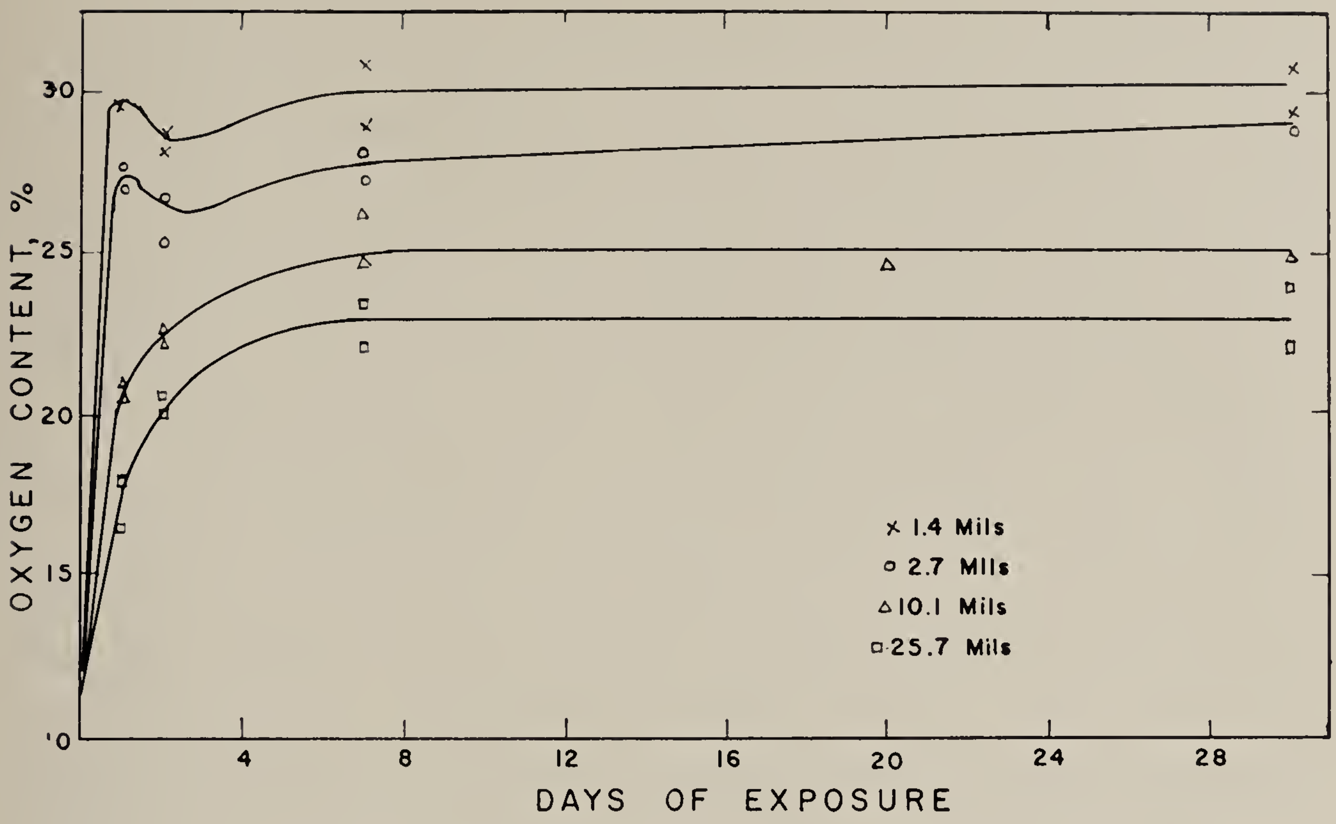

Fig. X-6. Oxygen content of PE linolenate films of graduated thicknesses.

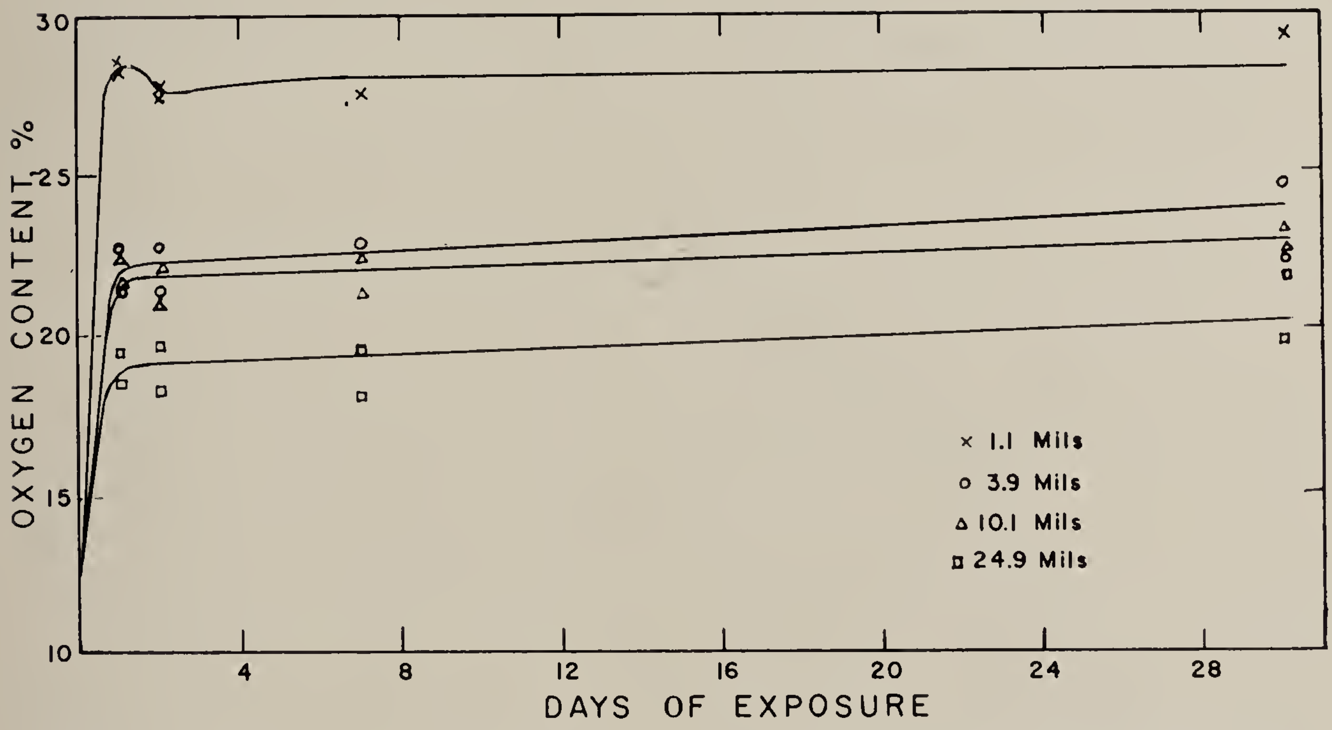

Fig. X-7. Oxygen content of diPE linolenate films of graduated thicknesses.

function of film depth. For the diPE linolenate film with which the attempt was made, the average of the upper 6 mils was 20.8%, whereas below a depth of 6 mils it was in the range of 17 to 18% (Table X-6).

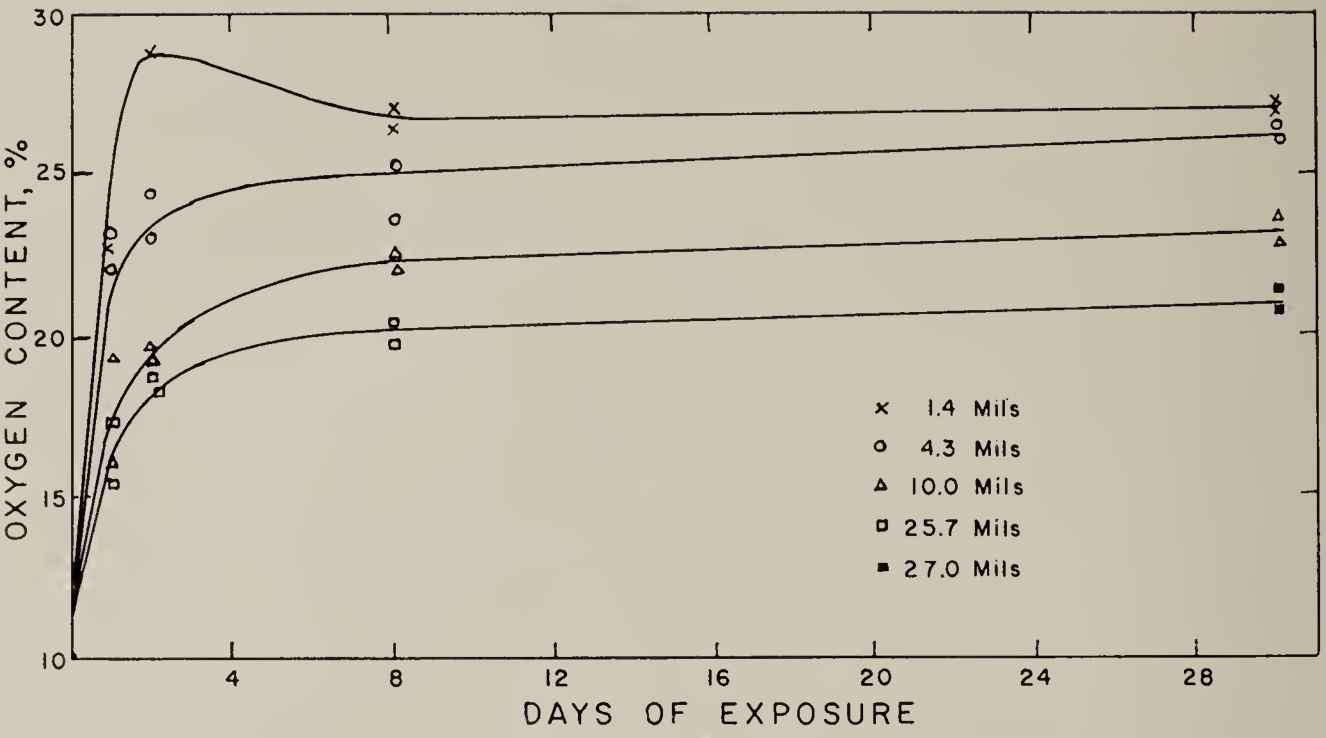

Fig. X-8. Oxygen content of varnish linseed oil films of graduated thicknesses.

The distribution of oxygen in this film can be approximated by establishing two limiting functions of oxygen concentration vs. film depth. In the first, the average oxygen concentration of each horizontal segment is assumed to be equal to that of a point midway in

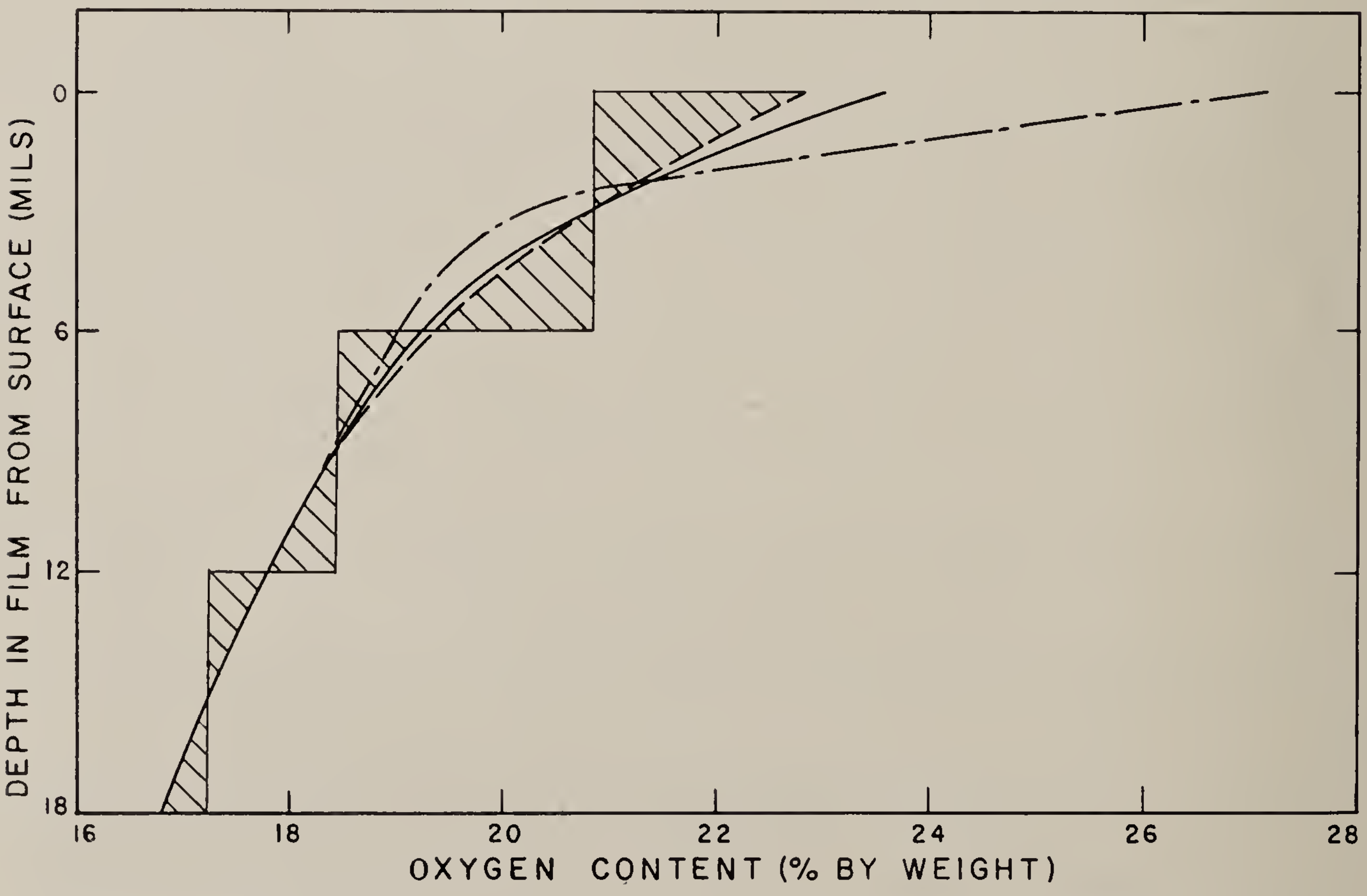

Fig. X-9. Oxygen content as a function of depth in film for DiPE linolenate.

each segment. Thus, this average for the 0 to 6 mils segment is the content at a point 3 mils deep, or 20.8% (Fig. X-9). Similarly, from Table X-6, the oxygen content at a point 9 mils below the surface is 18.7%, and at 15 mils, 17.2%. Considering the top segment, since 20.8 is a mean value, the shaded areas shown in the representation of that segment must be equal. The same reasoning applies for the middle and bottom segments, establishing the dashed curve.

Alternatively, assume that at the surface of this film the concentration of oxygen is the same (approximately 27%) as that of the 1.1 mil film of this vehicle after equal exposure. On the same principle of equal areas above and below the curve for each 6 mil segment, the distribution is that shown by the dash-dot curve, and the mean value of 20.8% oxygen is found to be at 1.8 mils below the film surface. Probability favors location of this value at some lesser depth than 3 mils; the actual curve would thus lie between these limiting conditions, possibly in the region shown by the solid line.

Discussion

Since only one compound was analyzed for oxygen content at different depths from the surface, no comparisons are possible of the influence of different fatty acids or alcohols of different functionality. The results do prove conclusively that film thickness is a determining factor in oxygen uptake. This fact alone is of great significance, since it emphasizes the difficulty of correlating values obtained on film studies with other physical and chemical observations.

Decomposition products remaining in the film appear to be responsible for total oxygen contents greater than theoretical. The amount of oxygen in the film at any given time is more than can be accounted for by gain in weight.

The title of this project, as used on the published report, is not quite accurate. Surface drying prevents further penetration of oxygen, and at best the total amount of oxygen determined is only the average of the relatively high content of the quick-drying surface layer and the vehicle in contact with the supporting surface. The varying amount of retained decomposition products, in proportion to film thickness, introduces further complications.

Shrinkage of Films, Project 20—University of Michigan

The literature has few data on the volumetric shrinkage of film-forming materials during the drying process. Sabin (4), Friend (2), and Carrick (1) had reported work bearing on some aspects of this problem.

Gauges were not acceptable tools in the present study, nor was a microscope. Their use involved destruction of the measured film area, or pressures sufficient to distort the film, or measurement of point rather than area thickness. In spite of the necessity of immersing the films in water for short periods, a water-displacement method was finally chosen to measure the volume changes accompanying the aging of films.

Experimental

The procedures in handling the vehicles and laying the films were as described above, except that all films were approximately 1.25 mils thick, and they were cast by the motor-driven applicator at a width of 2.5 inches on a row of four plate glass squares, each about 4 inches long and 0.04 inch thick. Only the two center squares of each 16-inch length of deposited film were used in obtaining the graphical data; the end-square films served for refractive index determinations and chemical analyses. Crawling, initially experienced with some of the compounds, appeared to be successfully overcome by treatment of the plates with the 5% solution of benzoic acid in alcohol.

Before the films were laid, the center glass squares were accurately weighed, and their volumes were determined from their water displacement by means of an analytical balance. The initial film thickness and volume were calculated from weight determinations, the known film area, and the specific gravity of the specimen material. The films were exposed for drying in a room of constant temperature and humidity under the specified conditions. Water displacement readings were made after 1, 2, 5, 10, etc., days on the analytical balance; on a particular day both of the duplicate panels were weighed in air, but alternate panels were immersed at each successive volume reading so as to reduce the number of water immersions per test film.

Results are summarized in Figs. X-10 to X-12 and Tables X-8 to X-14. There are two separate sets of volume and density curves for

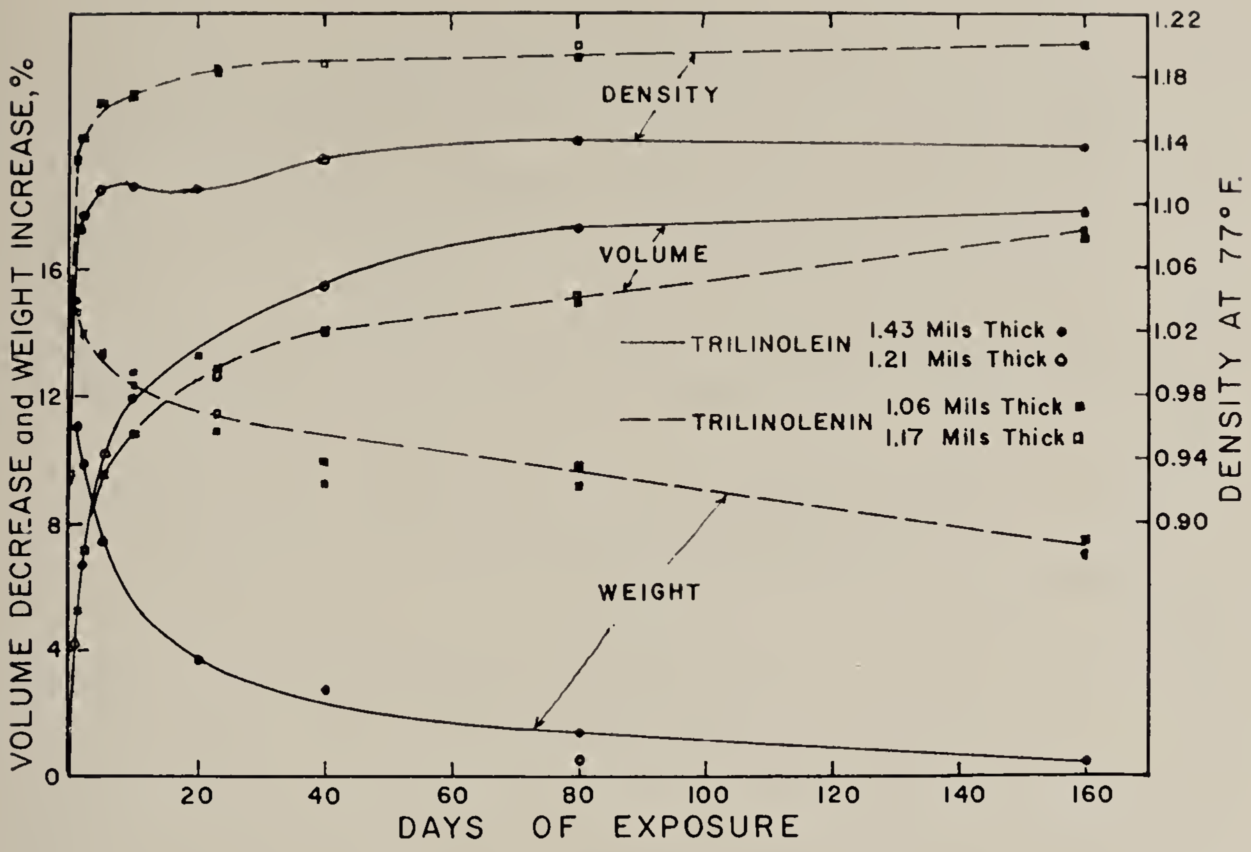

Fig. X-10. Changes in volume, weight, and density of trilinolein and trilinolenin films on aging.

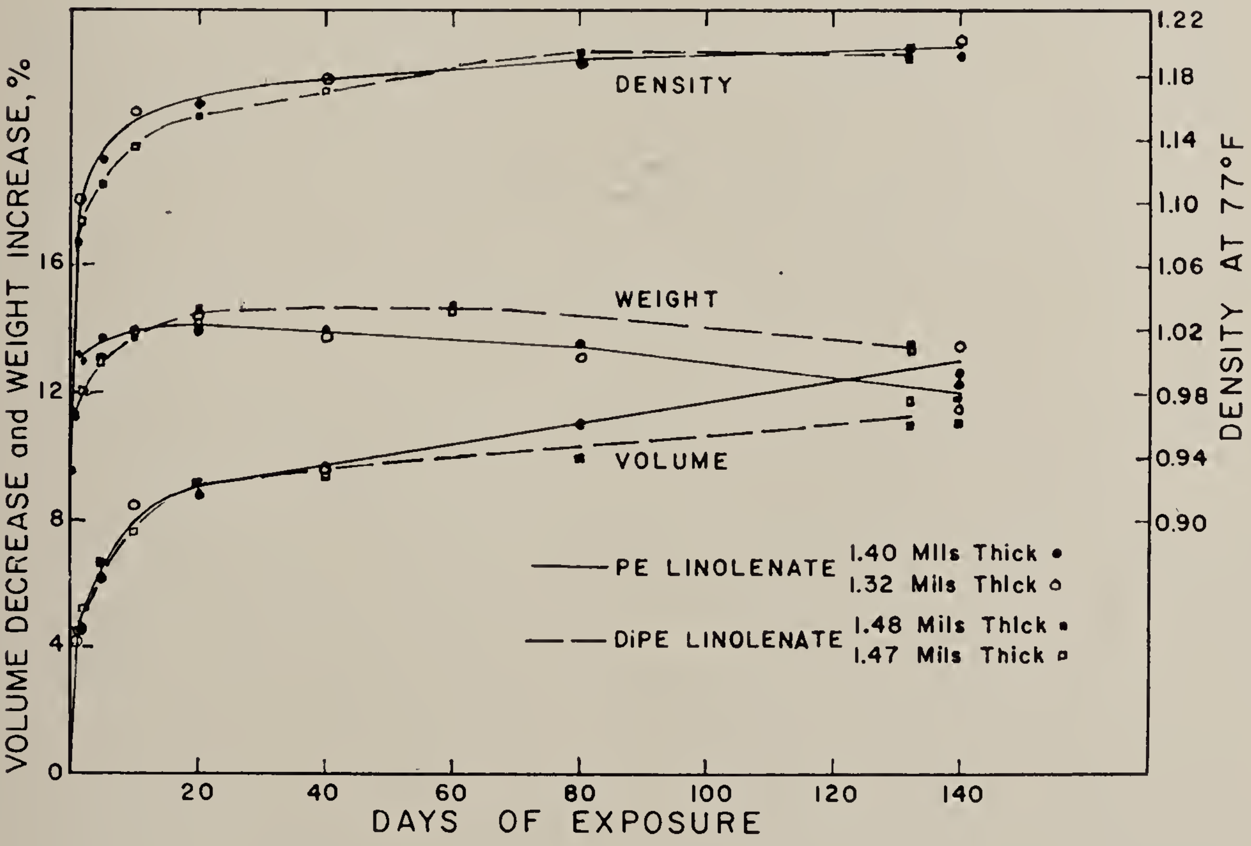

Fig. X-11. Changes in volume, weight, and density of PE and diPE linolenate films on aging.

varnish linseed oil in Fig. X-12. The data for this vehicle did not check as well as those for the other specimens, partly because the films suffered from some crawling and also because this oil served in the early experiments for improvement of techniques. This improvement brought about more consistent results in the subsequent tests.

Table X-10, containing the data on trieleostearin, was included in the report, although the volume changes shown were considered to be grossly in error. Films of this compound wrinkled and frosted severely, and the ridges and wrinkles apparently contained absorbed air, even though this was not noticeable as bubbles during the water immersion. This air caused the films to expand rather than shrink. For the 80- and 153-day figures, which are considered more nearly reliable, the experimental technique was modified: the plate and film were immersed in the regular water container, which was then placed under a bell jar at low pressure until all bubble evolution ceased (about 15 minutes) before the volume reading was taken. This modification was not put into use until the last stages of the study; it could not well have been used for the new films owing to the longer

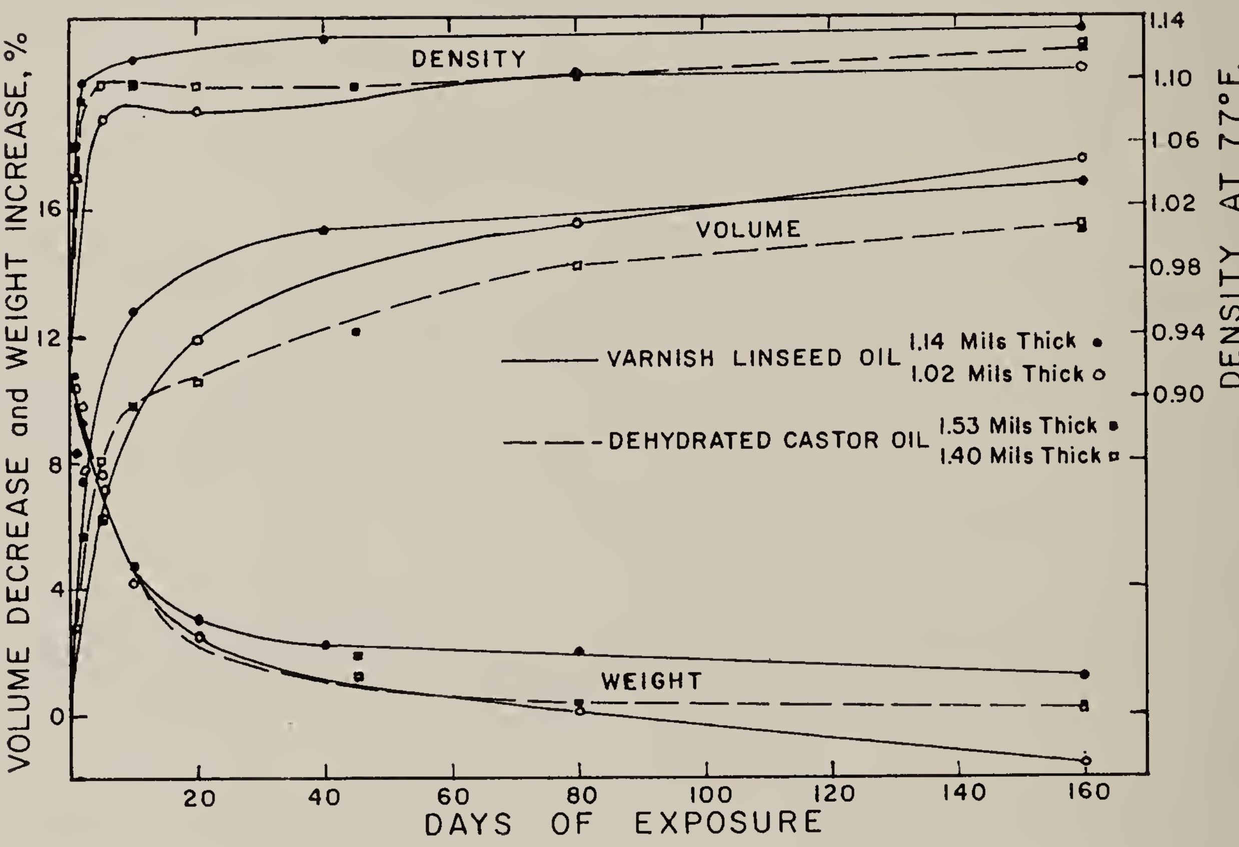

Fig. X-12. Changes in volume, weight, and density of linseed and dehydrated castor oil films on aging.

TABLE X-8

Shrinkage of Trilinolein Films

(Refractive index (on cellophane): 7 days, 1.4969; 90 days, 1.5018)

(Ultimate analysis of film (panel c, 1.37 mils thick, 7 days age): C, 63.85%; H, 9.59%; O, 26.56%)

Age (days)	Panel	Film thickness (mils)	% increase Wt.	% increase Vol.	Density, 77° F.
0	a	1.43			0.930
	b	1.21			0.930
	c	1.37			0.930
1	a		11.20	—	—
	b		11.17	−4.47	1.082
	c		11.21	—	—
2	a		9.66	−6.66	1.093
	b		9.51	—	—
	c		9.79	—	—
5	a		7.12	—	—
	b		7.21	−10.25	1.111
	c		7.49	—	—
7	c		6.87	—	—
10	a		5.49	−11.97	1.114
	b		5.46	—	—
20	a		3.63	—	—
	b		3.51	−13.37	1.111
40	a		2.99	—	—
	b		2.60	−15.51	1.130
80	a		1.41	−17.24	1.140
	b		0.55	—	—
160	a		0.59	−17.66	1.136
	b		0.35	−17.75	1.135

immersion required. Even the short (2 to 3 minutes) immersion used on the films in early stages caused some leaching of soluble material, since the immersed plate gained less than the panel not immersed on a particular day's reading. Long water immersion would be expected to affect the volume of such young films more strongly. The shrinkage values (16 to 17%) obtained on trieleostearin with the modified technique are in the same range as those for trilinolenin at 80 and 160 days.

TABLE X-9
Shrinkage of Trilinolenin Films
(Refractive index (on cellophane): 7 days, 1.5078; 80 days, 1.5097)
(Ultimate analysis of film (panel c, 1.35 mils thick, 7 days age): C, 63.60%; H, 8.84%; O, 27.56%)

Age (days)	Panel	Film thickness (mils)	% increase Wt.	% increase Vol.	Density, 77° F.
0	b	1.061			0.930
	x*	1.172			0.930
	c	1.345			0.930
1	b		14.81	−5.37	1.128
	x		14.10	—	—
	c		14.22	—	—
2	b		13.96	—	—
	x		13.89	−7.13	1.141
	c		13.46	—	—
5	b		13.26	−9.65	1.166
	x		13.63	—	—
	c		13.46	—	—
7	c		13.24	—	—
10	b		12.57	—	—
	x		12.81	−10.86	1.176
23	b		10.91	−12.98	1.185
	x		11.43	−12.77	1.188
40	b		9.30	—	—
	x		9.94	−14.00	1.189
80	b		9.20	−14.92	1.193
	x		9.84	−15.16	1.204
160	b		7.01	−17.26	1.203
	x		7.48	−16.87	1.202

* Original panel "a" replaced by panel "x" because film dried with irregular surface.

For the determinations of refractive index, one of the end glass squares had been covered with thin cellophane (approximately 0.9 mil thick) before laying the film, and the prescribed procedure was followed of cutting out a strip 12 × 26 mm. in area at the desired time intervals and placing it face down in intimate contact on the Abbé refractometer prism for the reading.

Ultimate analysis was run on a 0.15- to 0.20-gram sample, scraped from the other end square of each specimen after 7 days drying. The

TABLE X-10
Shrinkage of Trieleostearin Films
(Refractive index (on cellophane): 7 days, 1.5022; 80 days, 1.5040)
(Ultimate analysis of film (panel c, 1.40 mils thick, 7 days age): C, 62.45%; H, 6.76%; O, 30.79%)

Age (days)	Panel	Film thickness (mils)	% increase Wt.	% increase Vol.	Density 77° F.
0	a	1.352			0.930
	b	1.473			0.930
	c	1.398			0.930
1	a		10.81	37.35*	0.750
	b		10.21	—	—
	c		10.21	—	—
2	a		10.15	—	—
	b		10.05	28.26*	0.798
	c		10.05	—	—
5	a		8.79	10.22*	0.918
	b		8.25	—	—
	c		8.37	—	—
7	c		7.50	—	—
10	a		6.77	5.44*	0.942
	b		5.75	—	—
20	a		3.06	—	—
	b		2.45	9.93*	0.885
40	a		1.72	1.88*	0.946
	b		2.39	—	—
80	a		1.63	—	—
	b		1.80	−16.37	1.132
153	a		0.75	−16.22	1.119
	b		−0.35	−16.88	1.116

* These plus values are presumed erroneous but are included as part of the accumulated data, as mentioned in the text.

analytical procedure was the same as that used by Carrick and Snoddon.

Discussion

The curves of Figs. X-10 to X-12 are surprisingly smooth, considering that successive points are taken from alternate panels. This

TABLE X-11
Shrinkage of PE Linolenate Films
(Refractive index (on cellophane): 7 days, 1.5082; 80 days, 1.5115)
(Ultimate analysis of film (panel c, 1.08 mils thick, 7 days age): C, 63.53%; H, 8.77%, O, 27.70%)

Age (days)	Panel	Film thickness (mils)	% increase		Density, 77° F.
			Wt.	Vol.	
0	a	1.398			0.930
	b	1.322			0.930
	c	1.081			0.930
1	a		13.12	—	—
	b		13.10	−4.20	1.098
	c		13.66	—	—
2	a		12.97	−4.53	1.101
	b		12.93	—	—
	c		13.99	—	—
5	a		13.68	−6.19	1.127
	b		13.64	—	—
	c		14.27	—	—
7	c		14.52	—	—
10	a		13.61	—	—
	b		13.89	−8.48	1.157
20	a		13.83	−8.78	1.161
	b		14.31	—	—
40	a		13.90	—	—
	b		13.68	−9.57	1.169
80	a		13.60	−11.03	1.188
	b		13.05	—	—
140	a		12.27	−12.55	1.194
	b		11.55	−13.54	1.205

confirms the reliability of the method for studies of this type. Shrinkage was much greater than expected, and since the films remained attached to the glass plates, so that there could be no change in area, it must necessarily represent a diminution of thickness. Although final volume shrinkage values for all these specimens lay within a fairly narrow range, there was considerable variation in their total gain in weight. (Weight gain curves in these figures begin at the age of 1 day; no attempt was made to observe the change in

TABLE X-12
Shrinkage of DiPE Linolenate Films
(Refractive index (on cellophane): 7 days, 1.5092; 80 days, 1.5110)
(Ultimate analysis of film (panel c, 1.51 mils thick, 7 days age): C, 63.95%; H, 8.47%; O, 27.58%)

Age (days)	Panel	Film thickness (mils)	% increase		Density, 77° F.
			Wt.	Vol.	
0	a	1.480			0.930
	b	1.473			0.930
	c	1.510			0.930
1	a		11.31	−4.52	1.084
	b		11.01	—	—
	c		11.07	—	—
2	a		11.48	—	—
	b		11.21	−5.55	1.095
	c		11.25	—	—
5	a		11.77	−6.30	1.109
	b		11.81	—	—
	c		11.71	—	—
7	c		12.25	—	—
10	a		13.10	—	—
	b		12.78	−7.46	1.133
20	a		14.05	−8.35	1.157
	b		13.91	—	—
40	a		14.39	—	—
	b		14.23	−9.52	1.174
80	a		14.84	−9.94	1.186
	b		14.76	−10.31	1.190
132	a		13.76	−11.18	1.191
	b		13.35	−11.96	1.197

weight for the first 24 hours.) It may be noted that diPE linolenate, which showed the smallest shrinkage value, was the compound which wrinkled least in thick layers in Project 18. Yet trieleostearin, which, as expected, wrinkled most in that study, shrank (according to final figures) only about as much as linseed oil, trilinolein, and trilinolenin. Dehydrated castor oil, another vehicle with known wrinkling tendencies, shrank a little less than these.

Carrick and Permoda ascribed the shrinkage to by-product evolution and other changes during the complex chemical reactions of

TABLE X-13

Shrinkage of Varnish Linseed Oil Films

(Refractive index (on cellophane): 7 days, 1.4934; 90 days, 1.4990)

(Ultimate analysis of film (panel c, 1.42 mils thick, age 7 days): C, 63.90%; H, 9.45%; O, 26.65%)

Age (days)	Panel	Film thickness (mils)	% increase		Density, 77° F.
			Wt.	Vol.	
0	a	1.135			0.932
	b	1.015			0.930
	c	1.415			0.932
1	a		10.81	—	—
	b		10.46	—	—
	c		10.77	—	—
2	a		9.26	−7.43	1.106
	b		9.87	—	—
	c		10.26	—	—
5	a		7.17	—	—
	b		7.66	−7.18	1.079
	c		9.25	—	—
10	a		4.49	−12.82	1.117
	b		4.29	—	—
20	a		3.10	—	—
	b		2.57	−11.91	1.083
40	a		2.35	−15.36	1.127
	b		0.00	—	—
80	a		2.09	—	—
	b		0.12	−15.56	1.105
160	a		1.18	−16.66	1.132
	b		−1.65	−17.49	1.108

oxidation and polymerization, and perhaps as well to a progressive compaction of the gel structure. So few compounds were investigated in this project that no basis was established for valid conclusions either as to the influence on shrinkage of degree of unsaturation of acids or functionality of alcohols; however, the unexpected magnitude of the volume changes is a finding of great interest.

TABLE X-14
Shrinkage of Dehydrated Castor Oil Films
(Refractive index (on cellophane): 7 days, 1.4958; 90 days, 1.4990)
(Ultimate analysis of film (panel c, 1.98 mils thick): age 7 days: C, 60.76%; H, 10.52%; O, 28.72%; age 64 days: C, 64.15%; H, 9.06%; O, 26.79%)

Age (days)	Panel	Film thickness (mils)	% increase Wt.	% increase Vol.	Density, 77° F.
0	a	1.526			0.946
	b	1.404			0.950
	c	1.978			0.950
1	a		8.35	—	—
	b		8.43	−2.82	1.060
	c		7.14	—	—
2	a		8.15	−5.73	1.085
	b		7.84	—	—
	c		7.40	—	—
5	a		6.26	—	—
	b		6.35	−8.01	1.099
	c		6.50	—	—
7	c		6.29	—	—
10	a		4.78	−9.80	1.099
	b		4.86	—	—
20	a		3.41	—	—
	b		3.43	−10.48	1.098
45	a		1.93	−12.15	1.098
	b		1.25	—	—
80	a		0.44	—	—
	b		0.11	−14.17	—
160	a		0.28	−15.31	1.120
	b		0.09	−15.49	1.123

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CHAPTER XI

Stress-Strain Properties

Long-lasting protection by a paint film depends on its integrity or strength or cohesion, including the ability to expand or contract along with the surface on which it is applied; and on its continued adherence to that surface. Unfortunately, the project (No. 11) the purpose of which was to measure quantitatively this latter property for the Federation compounds could not be carried out, as was explained in Chapter I. Qualitative indications of adhesive property reported in Projects 8, 13, and 17 on outdoor and accelerated weathering are not dependable. This is because of the probability that in many cases an invisible repellent monomolecular film of some kind was present or formed on the surfaces of the glass plates at the time of application of the specimens, preventing establishment of a proper bond.

Project 4, on Stress-Strain Properties, dealt with the flexibility or, more properly, the distensibility (response to stress) of clear and pigmented films as a function, under specified conditions, of their age. Wood, metal, and other substrates shrink or expand appreciably with changes in temperature or in moisture content, and it was hoped to learn how a choice of composition of vehicles might best enable paints to accommodate themselves to such shrinkage or expansion. Distensibility is especially important in the special case of coatings for the metal decorating industry. Applied on flat sheets, baked, and then sometimes held for as long as six months before forming, these decorations must stand drastic stretching, bending, and compression when the sheets are drawn into screw-caps and other intricate shapes.

Stress-Strain Properties, Project 4—Philadelphia Club

Dr. A. C. Elm conducted this study in the laboratories of the New Jersey Zinc Co. (of Pennsylvania) at Palmerton, Pennsylvania. His report was published in the *Official Digest,* No. 322, 701 (November, 1951), but by an error of transcription which was not discovered by him until some time later, the stress-strain curves in the appendices of that report indicate loads four times as high as they should be. Since these curves were used only for comparisons, the error did not affect the conclusions drawn.

Limitations of space, apparatus, and manpower made it necessary to examine the clear and the pigmented specimens in two separate campaigns and to restrict the number of individual materials in each to 12:

Varnish linseed oil
Commercial alkyd
Trilinolein
Trilinolenin
Trieleostearin
PE linoleate
PE linolenate
PE eleostearate
LO linoleic glycerol alkyd
LO linolenic glycerol alkyd
SO linoleic glycerol alkyd
SO linolenic glycerol alkyd

Experimental

Plate glass panels, 4 × 6 inches, were prepared by silvering one side in the following manner, distilled water being used throughout. They were thoroughly cleaned with chromic acid solution, rinsed with water, and while still wet rubbed with a paste of whiting and water, rinsed again, and sensitized by rubbing the surface with a dilute (1 to 5%) solution of stannous chloride acidified with a few drops of hydrochloric acid. They were rinsed once more with water and immediately treated with the silvering solution while lying level on a thick pad of wet cloth or felt in a tray maintained at 50° C. The solution was poured on carefully, building up as thick a layer as the plates would retain. After 8 to 10 minutes, the panels were removed, drained, rinsed, and allowed to dry. The operator wore clean rubber gloves for all handling of the plates.

For each three panels there was required a fresh mixture of 10 ml. each of filtered portions of the two stock solutions and 128 ml. of distilled water. Solution A contained 40 grams of silver nitrate in

480 grams water, with enough ammonia water added to dissolve almost, but not quite, all of the brown precipitate that formed at first; Solution B contained 14 grams Epsom salt ($MgSO_4 \cdot 7H_2O$) and 160 grams Rochelle salt ($KNaC_4H_4O_6 \cdot 4H_2O$) in 448 grams water.

The Federation samples were treated with drier and aged as prescribed. Films were laid on the silvered surface by means of a spreader the clearance of which was adjusted to yield, after drying, clear films 1.25 mils and pigmented films 2 mils thick. After drying one week under the specified conditions, they were stripped by amalgamation and cut to the desired specimen size ($^1/_2 \times 5$ inches). They continued to age under the same conditions until tested for stress-strain properties 2, 4, 8, 16, and 32 weeks after preparation. The clear specimens were also tested at 52 weeks, but it was found that the rate of change was so slight after 32 weeks that it was believed unnecessary to continue study of the pigmented compounds for the full year.

The stress-strain apparatus, consisting of a conditioning cabinet and a testing chamber, is shown in Fig. XI-1. It had been satisfactorily used in a number of similar investigations. At the side of the conditioning cabinet (Fig. XI-2) a Siroco blower circulated air over a copper coil (not shown) to cool it to slightly below the desired temperature and to remove some of the moisture. An electrical heater brought the air back to temperature, and trays containing a selected salt solution insured the desired relative humidity at that temperature. The air then passed over the test specimens, through the testing chamber, and back to the copper cooling coil.

The testing apparatus (Fig. XI-3) consisted of three main parts whose functions were (*1*) applying load to the test specimen, (*2*) recording the elongation-load curve, and (*3*) maintaining proper temperature and humidity around the specimen. The portion of the apparatus by means of which the load was applied is sketched in Fig. XI-4. The specimen, which had a cross-sectional area of 0.000625 sq. inch or 0.4 sq. mm., was suspended from a fixed support by means of a clamp. A mercury receiver was attached by a second clamp to the lower end of the specimen and was exactly counterbalanced as shown so that there was no load on the film when the receiver was empty. Mercury applied the load by flowing into the receiver at a constant, predetermined rate assured by a calibrated orifice through which it was forced by a hydrostatic head maintained uniform by an overflow arrangement.

The elongation of the specimen was followed by a microscope whose cross hairs were focused on a single bench mark on the test piece. A pen, coupled through a screw arrangement to the microscope (Fig. XI-5), recorded its vertical motion on a movable chart. The chart was driven by a synchronous motor so that its rate of travel corresponded to the rate of loading, while the microscope was actuated by a hand wheel coupled to the long vertical screw which

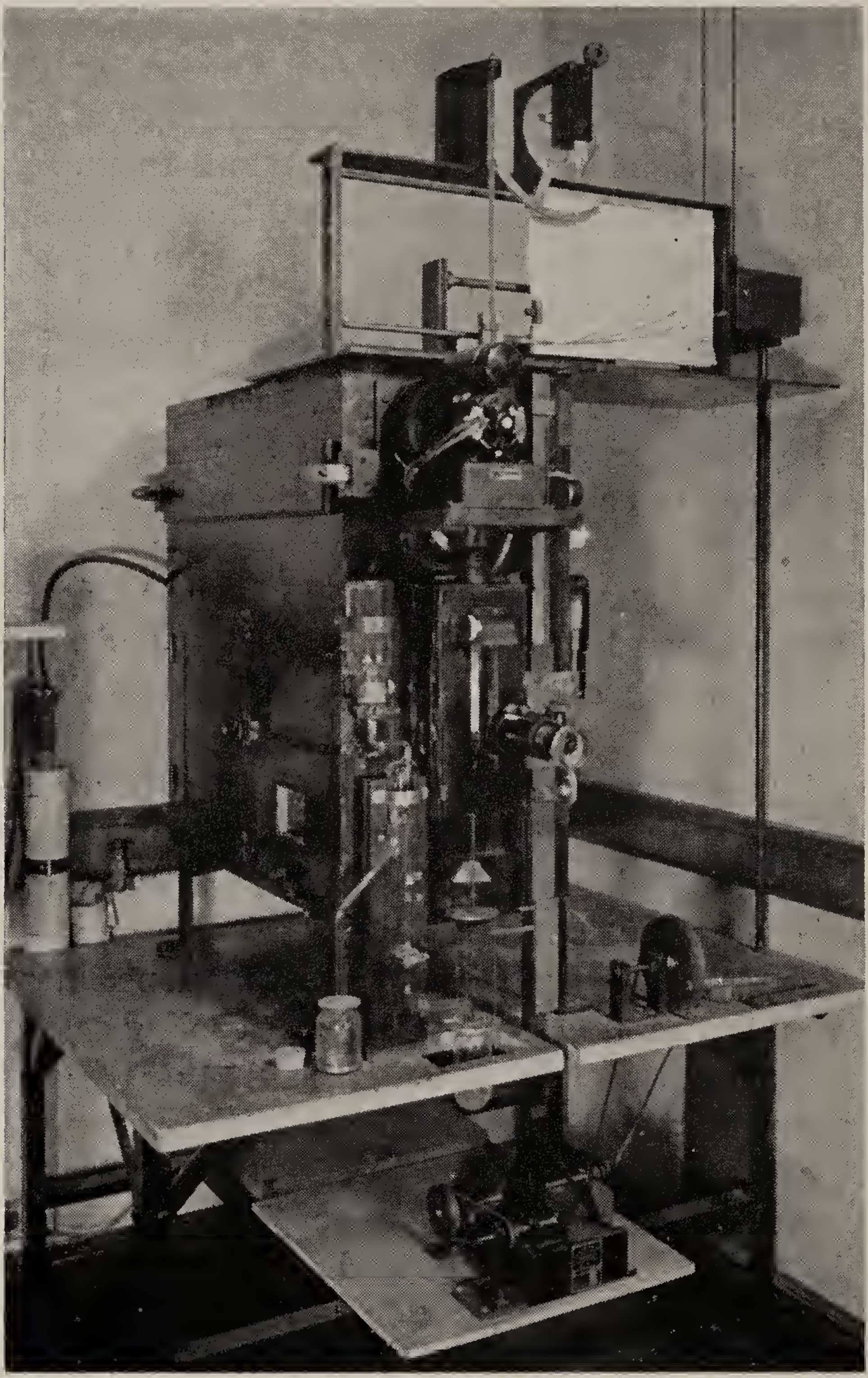

Fig. XI-1. Stress-strain apparatus.

carried it. Thus a direct stress-strain curve was drawn on the chart by the pen. A typical set of such curves from four specimens of the same film appears in Fig. XI-6.

The stress-strain data of three or four specimens obtained in this manner were then averaged, and the load values converted from grams per 0.4 sq. mm. to kilograms per square centimeter cross-sectional area. The results were plotted against elongation; but in the report as it appeared in the *Official Digest* (No. 322), although the abscissas of the stress-strain curves were marked as "load in kg. per cm.^{2}," the curves themselves were the original ones representing "grams per 0.4 mm.^{2}" This was the error above mentioned. To correct the values shown, the respective abscissa indices must be divided by

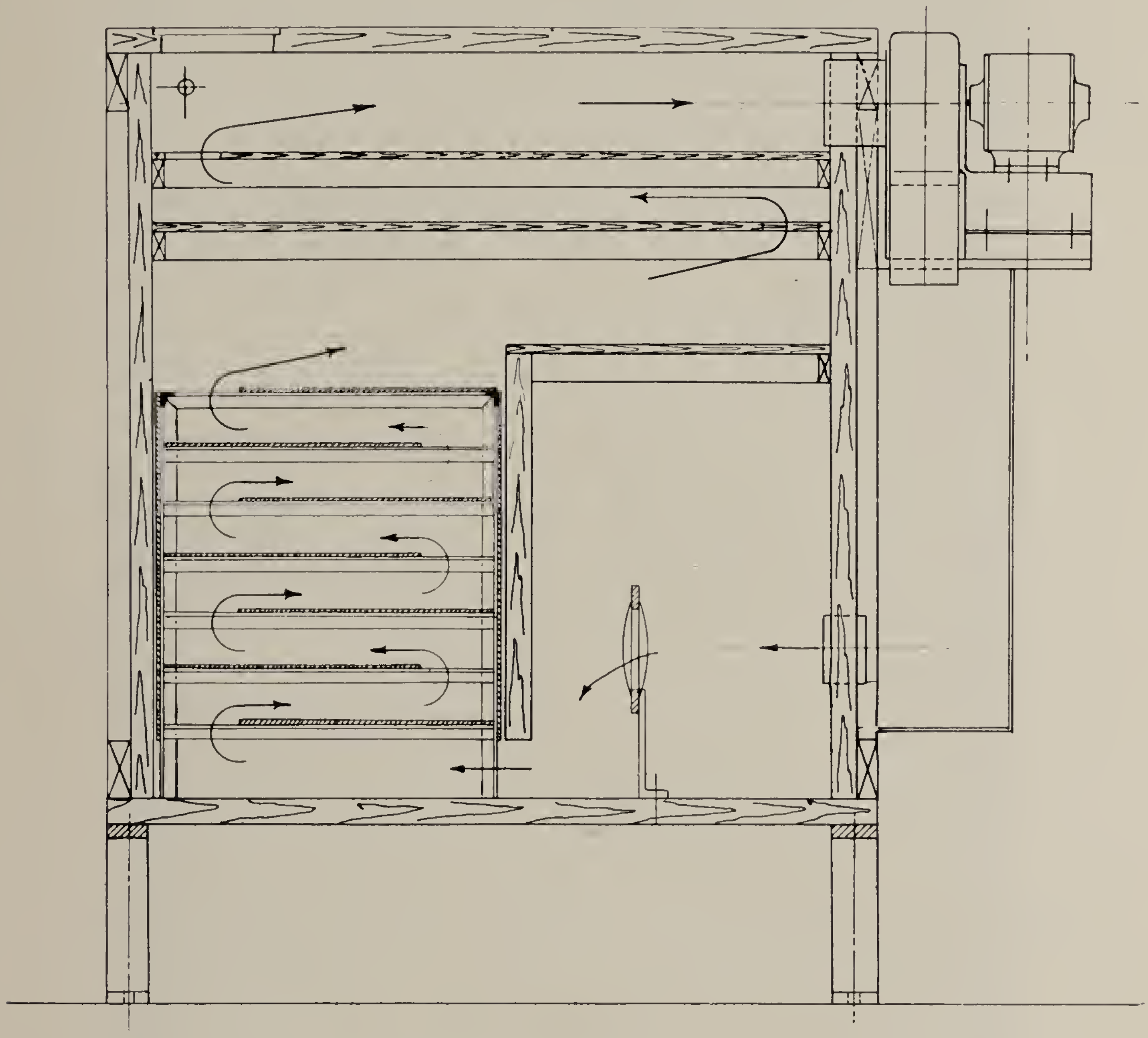

Fig. XI-2. Conditioning cabinet.

four, and this has been done in the graphs (Figs. XI-7 to XI-24) here shown; relative distensibility ordinates in Figs. XI-25 to XI-28 have been similarly corrected. As stated above, the curves were used only for comparisons which are unaffected by the absolute values. The clear films of the simple esters gave curves which varied so irregularly at different ages that only the plot for trilinolein, Fig. XI-7, is presented, as typical of that series.

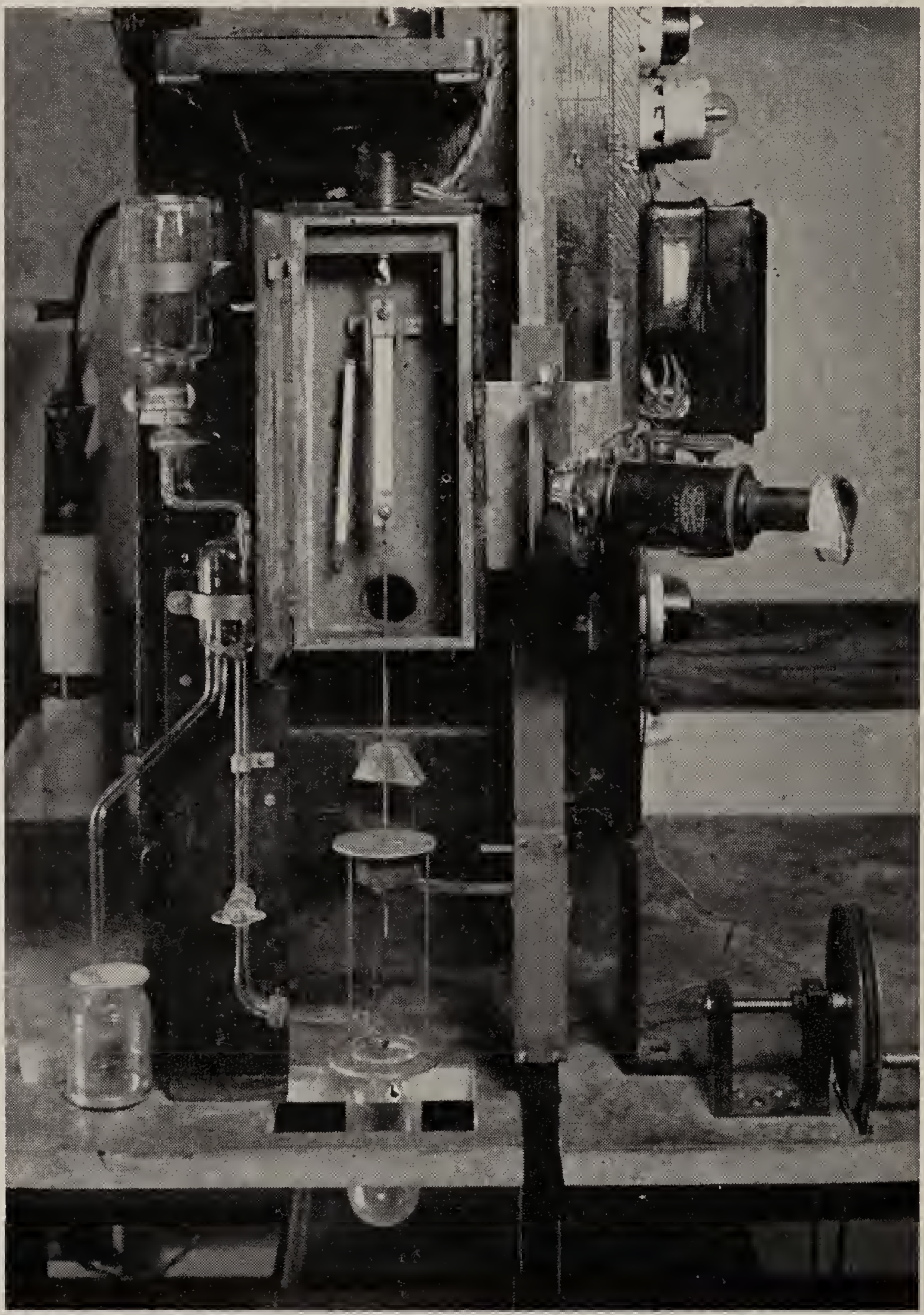

Fig. XI-3. Stress-strain testing unit.

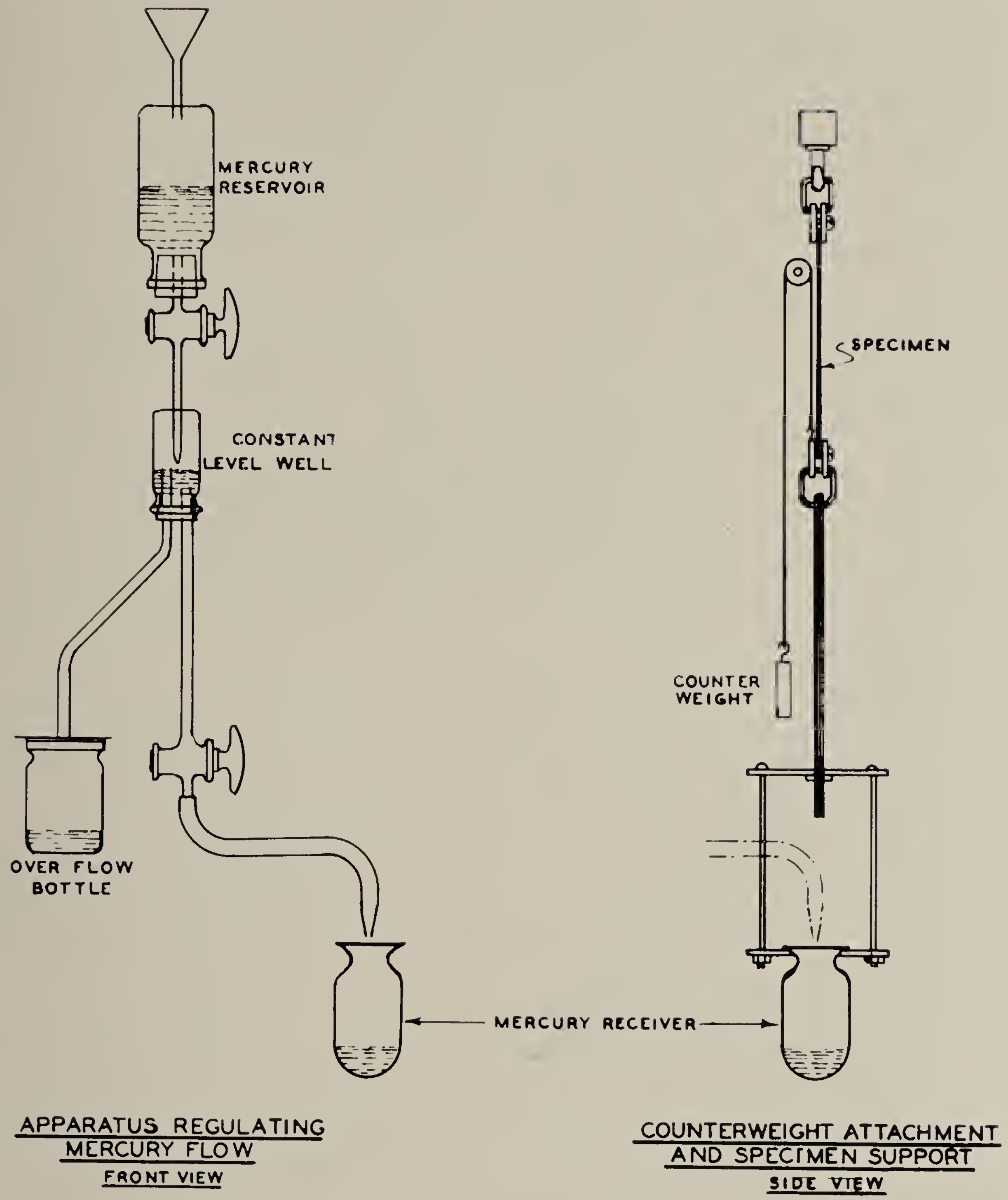

Fig. XI-4. Assembly of loading device.

Discussion

A complete stress-strain diagram, taking into account all the necessary conditions under which a film should be tested to determine its behavior in actual service, would be three dimensional. In this study all the tests were run under one standard set of conditions of temperature, humidity, and rate of loading (90 grams per minute). With only this single set of variables for the various films explored, it would be misleading to apply the conclusions to any other conditions.

Not only must organic coatings withstand a wide range of temperature and humidity variations, but also (as is not so generally appreciated) they are subject to an assortment of shock conditions which vary widely in the rate at which the shock is applied; this rate factor often has greater influence than the final stress the coating must withstand. The films with which the paint industry deals are not rigid solids with well-defined yield points, but are plastic materials with widely different yield and flow patterns which greatly

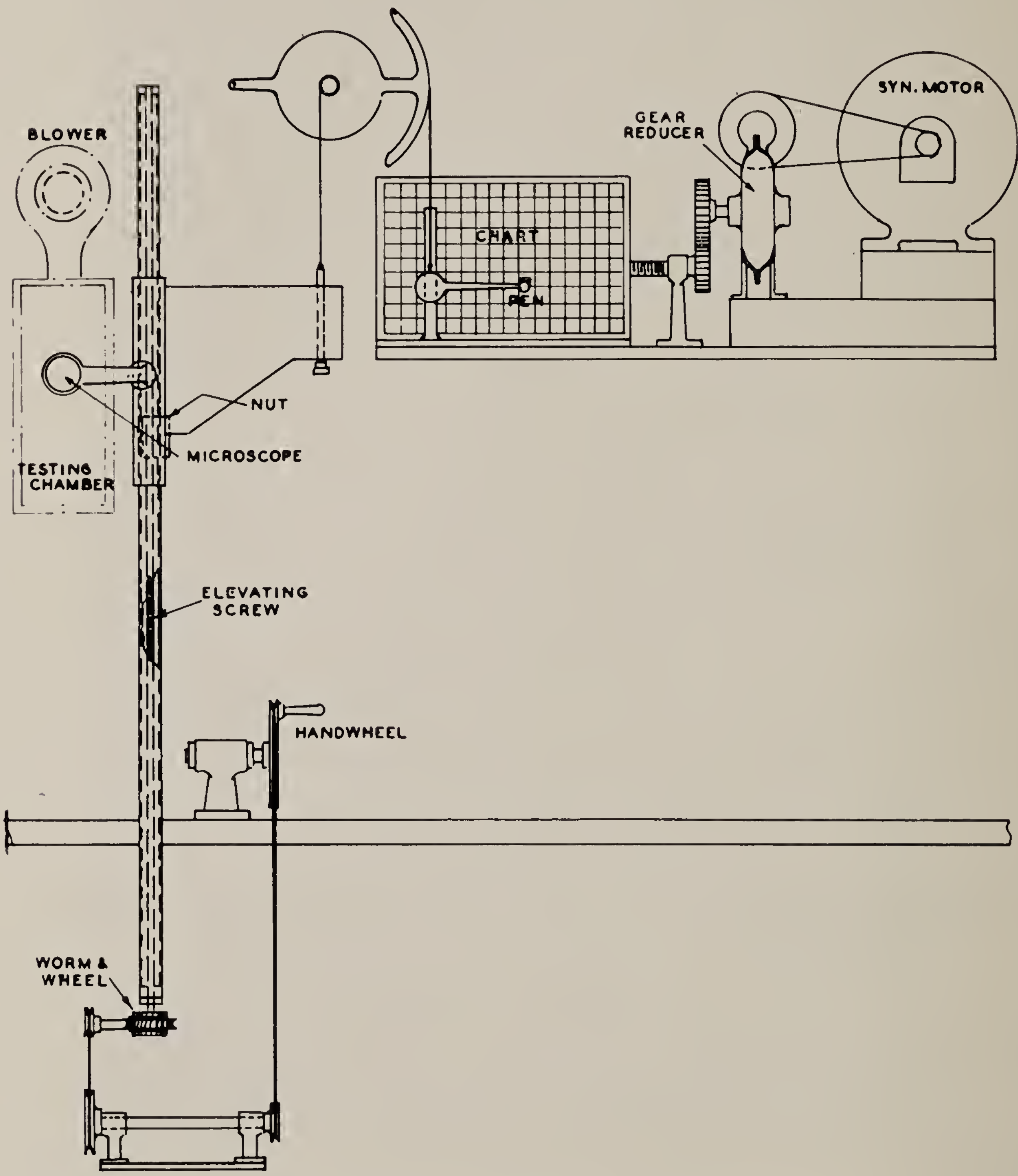

Fig. XI-5. Device for recording the stress-strain curve.

modify their ability to withstand stresses without rupture. When given enough time, films will meet external stresses by plastic deformation. If the time is too short, flow is too slow and rupture must occur.

The best that can be done with the data of this study is to gain an idea of the probable behavior of the materials investigated, under a closely limited set of conditions; generalizations outside of these would be undependable, even dangerous. Nevertheless, the results contributed materially to our understanding of what makes films behave as they do.

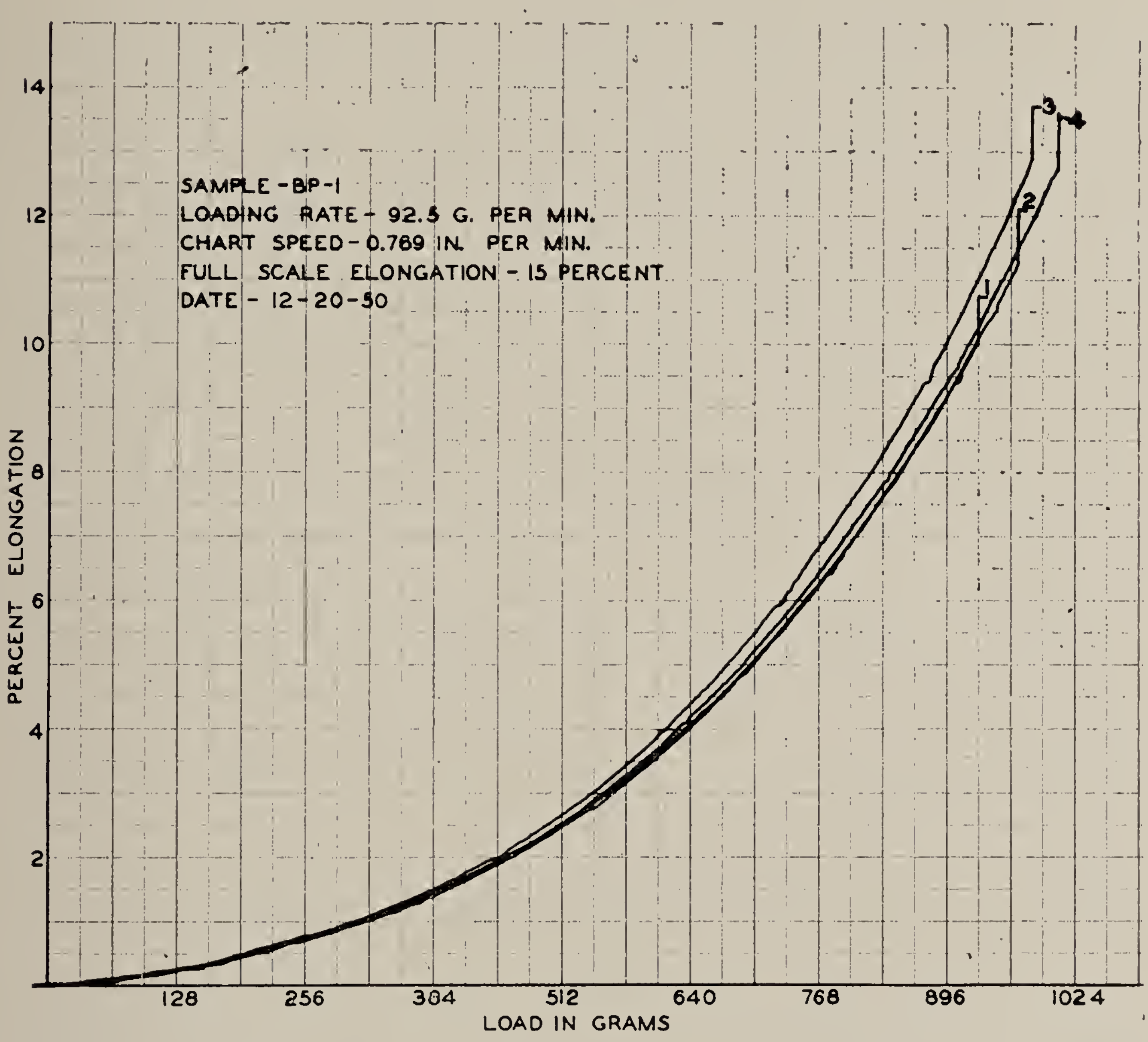

Fig. XI-6. Typical stress-strain curves from four specimens of the same film.

The two most interesting features of a stress-strain plot are the tensile strength (the load required to rupture the specimen), and the shape of the elongation-load curve. Several factors not readily amen-

Figs. XI-7 to XI-18 follow.
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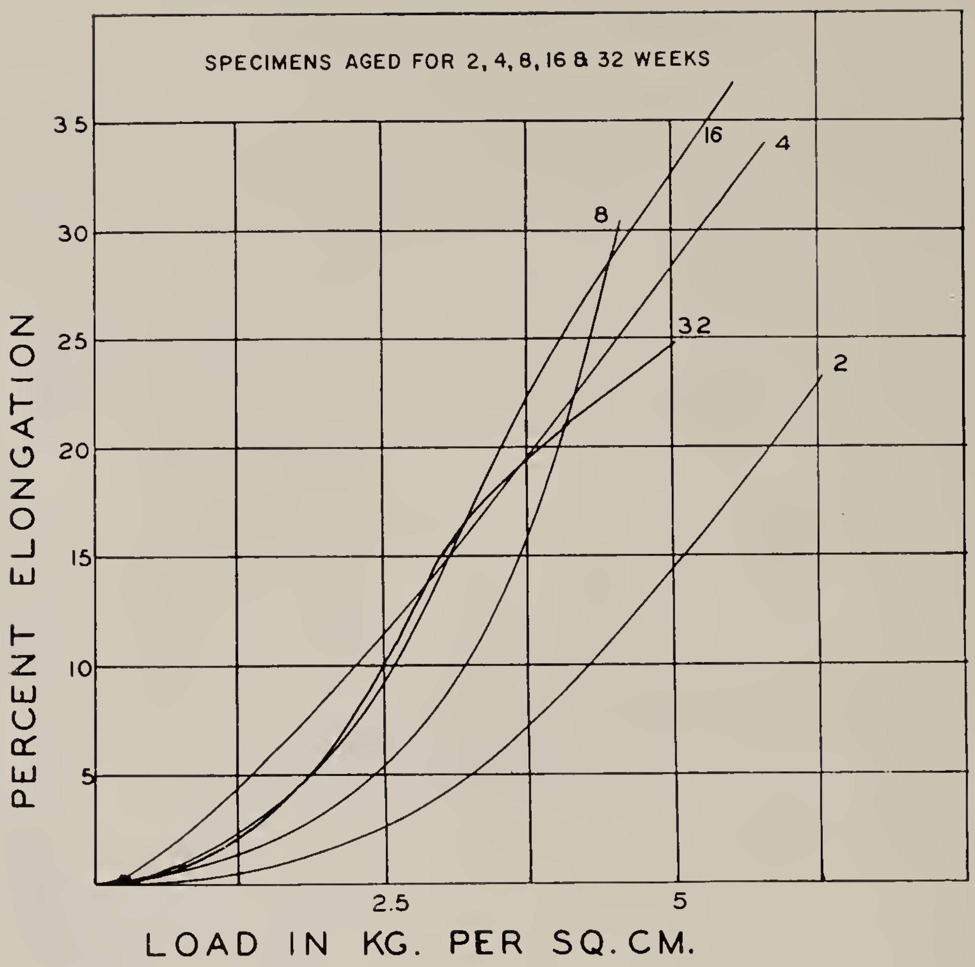

Fig. XI-7. Stress-strain properties of clear trilinolein films.

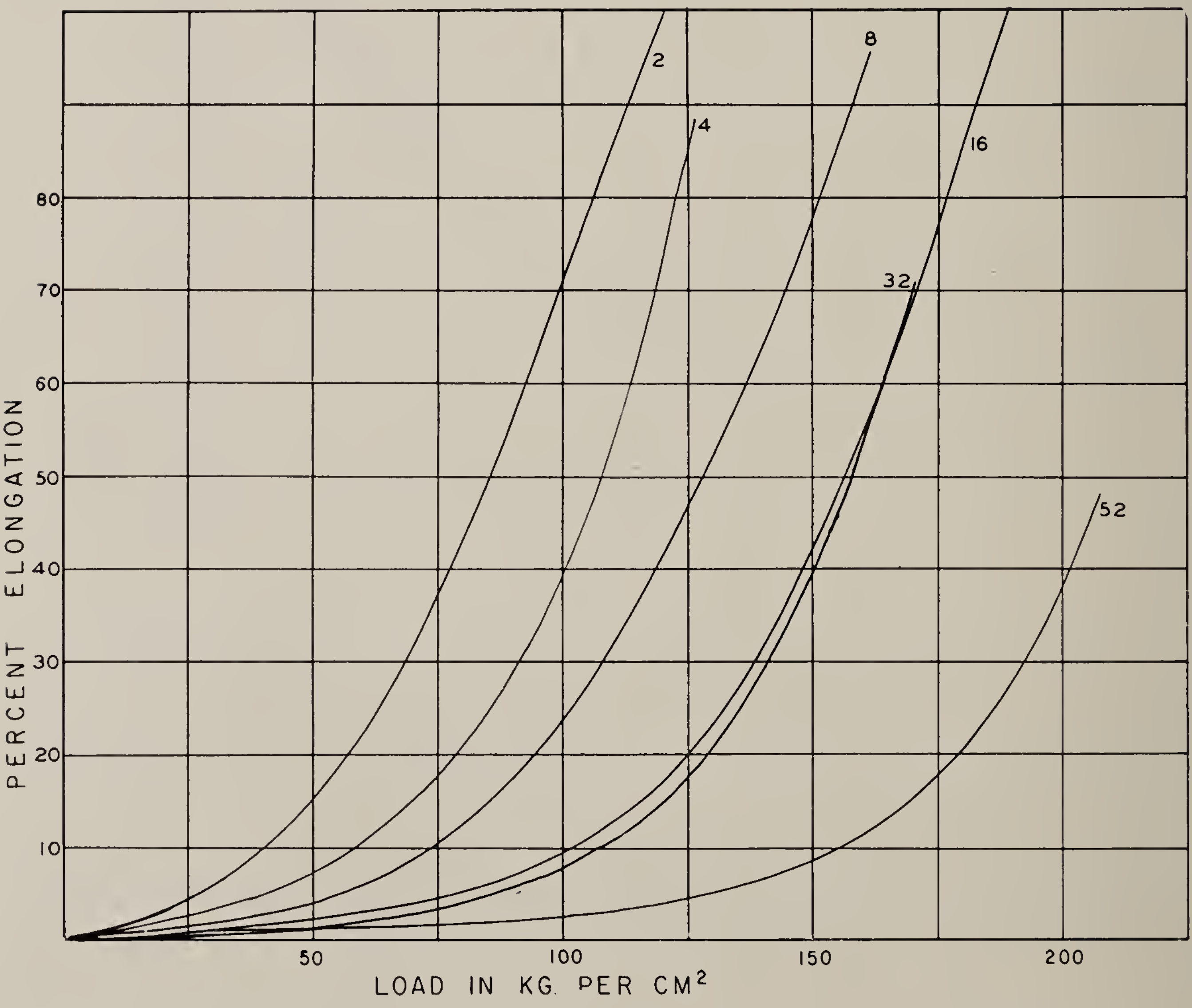

Fig. XI-8. Stress-strain properties of clear LO linoleic glycerol alkyd films.

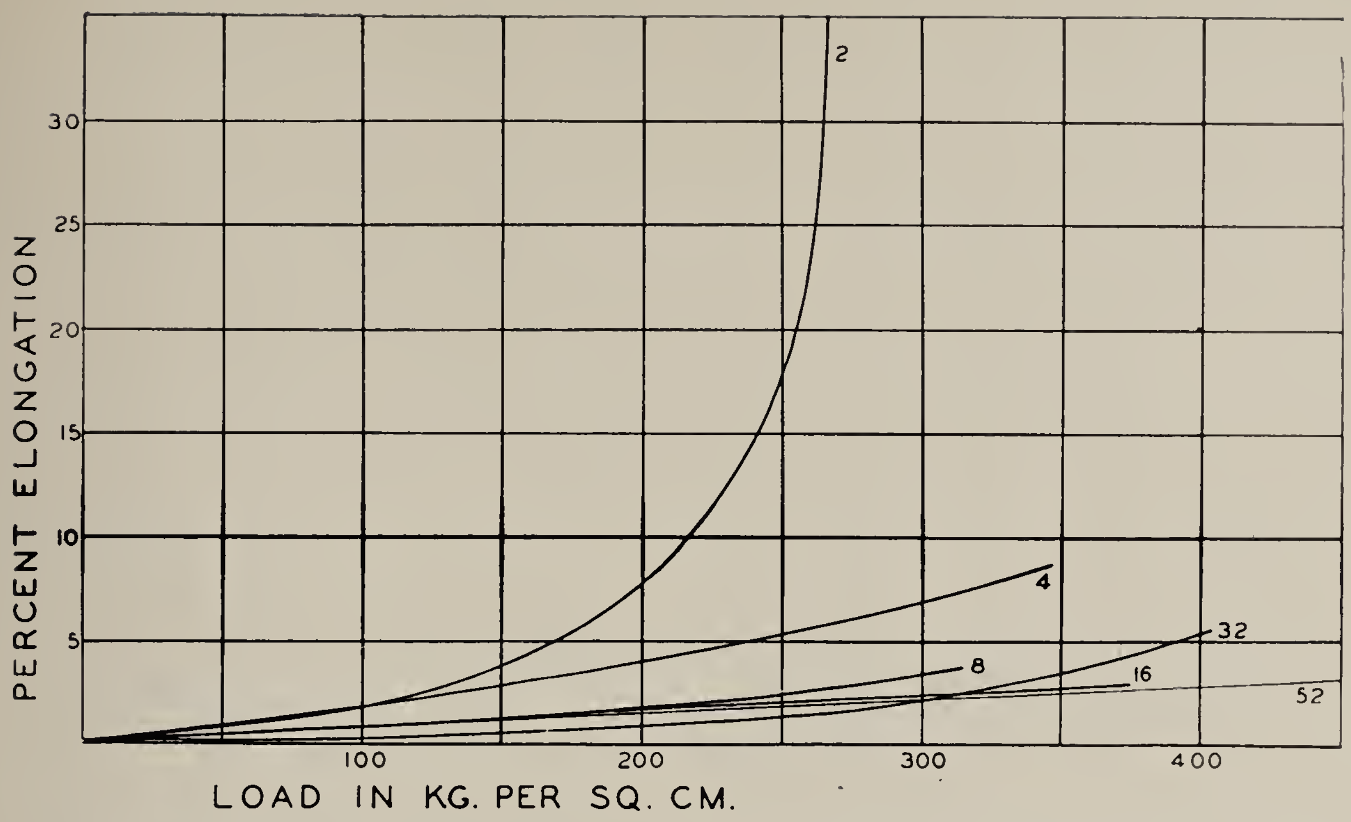

Fig. XI-9. Stress-strain properties of clear LO linolenic glycerol alkyd films.

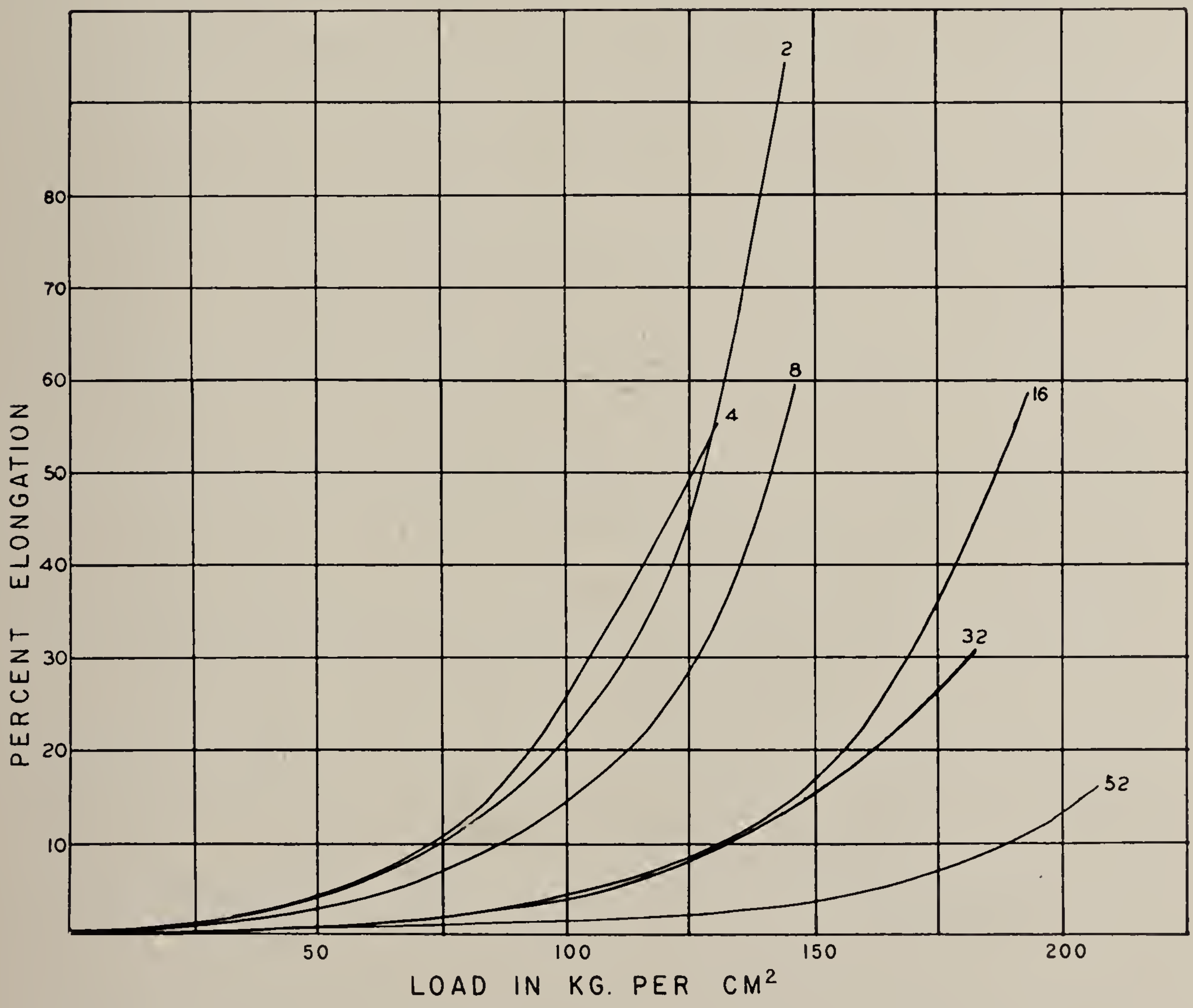

Fig. XI-10. Stress-strain properties of clear SO linoleic glycerol alkyd films.

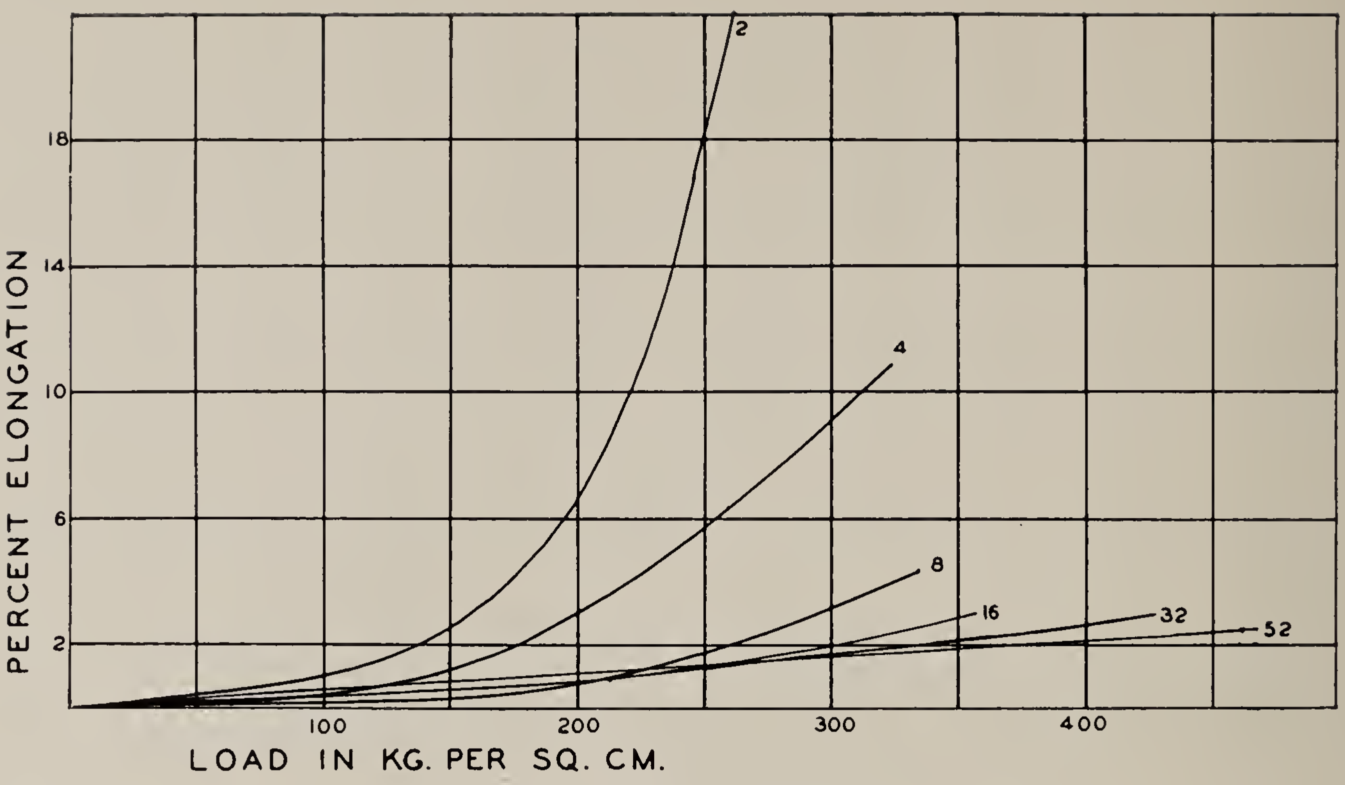

Fig. XI-11. Stress-strain properties of clear SO linolenic glycerol alkyd films.

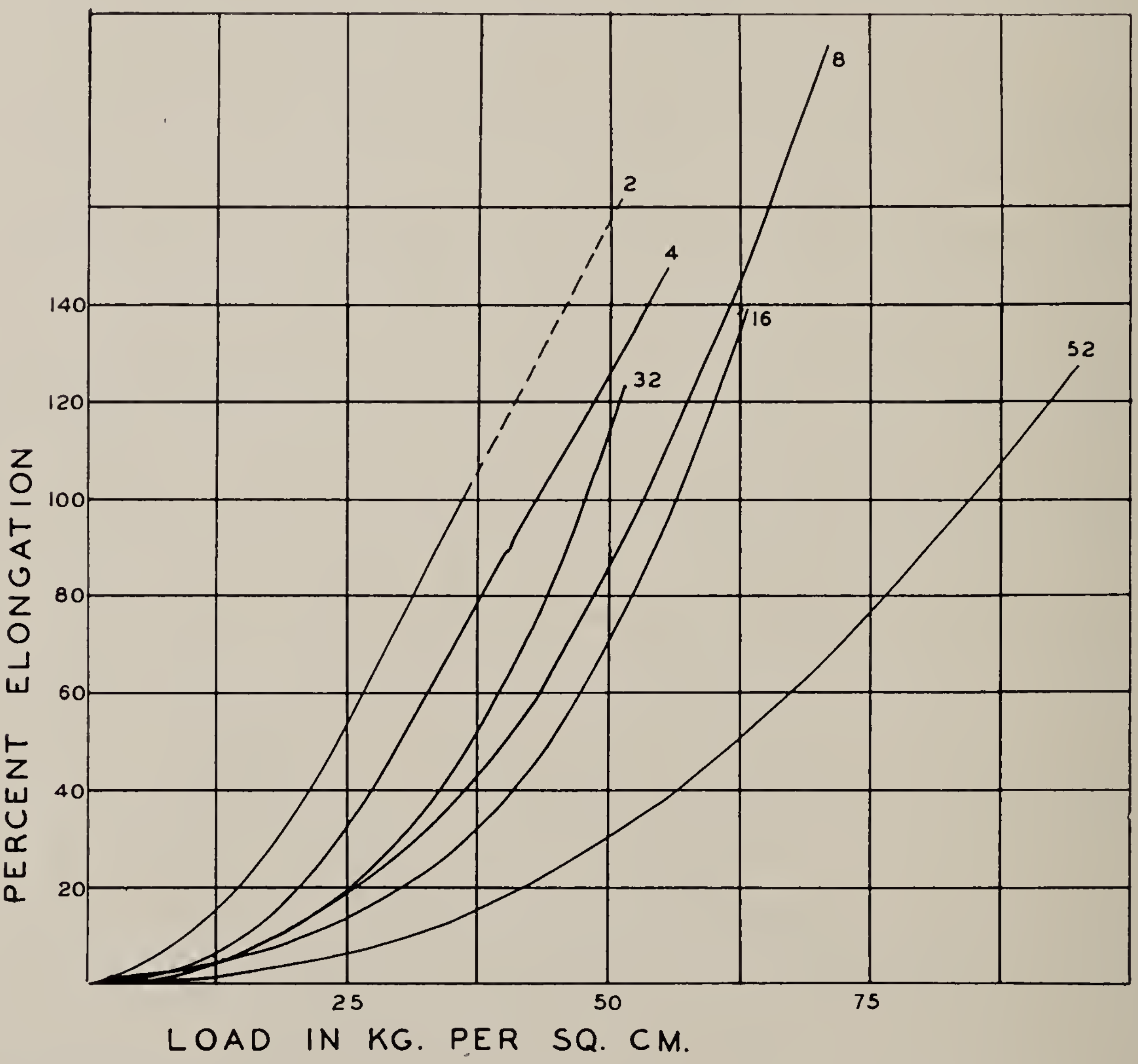

Fig. XI-12. Stress-strain properties of clear commercial alkyd films.

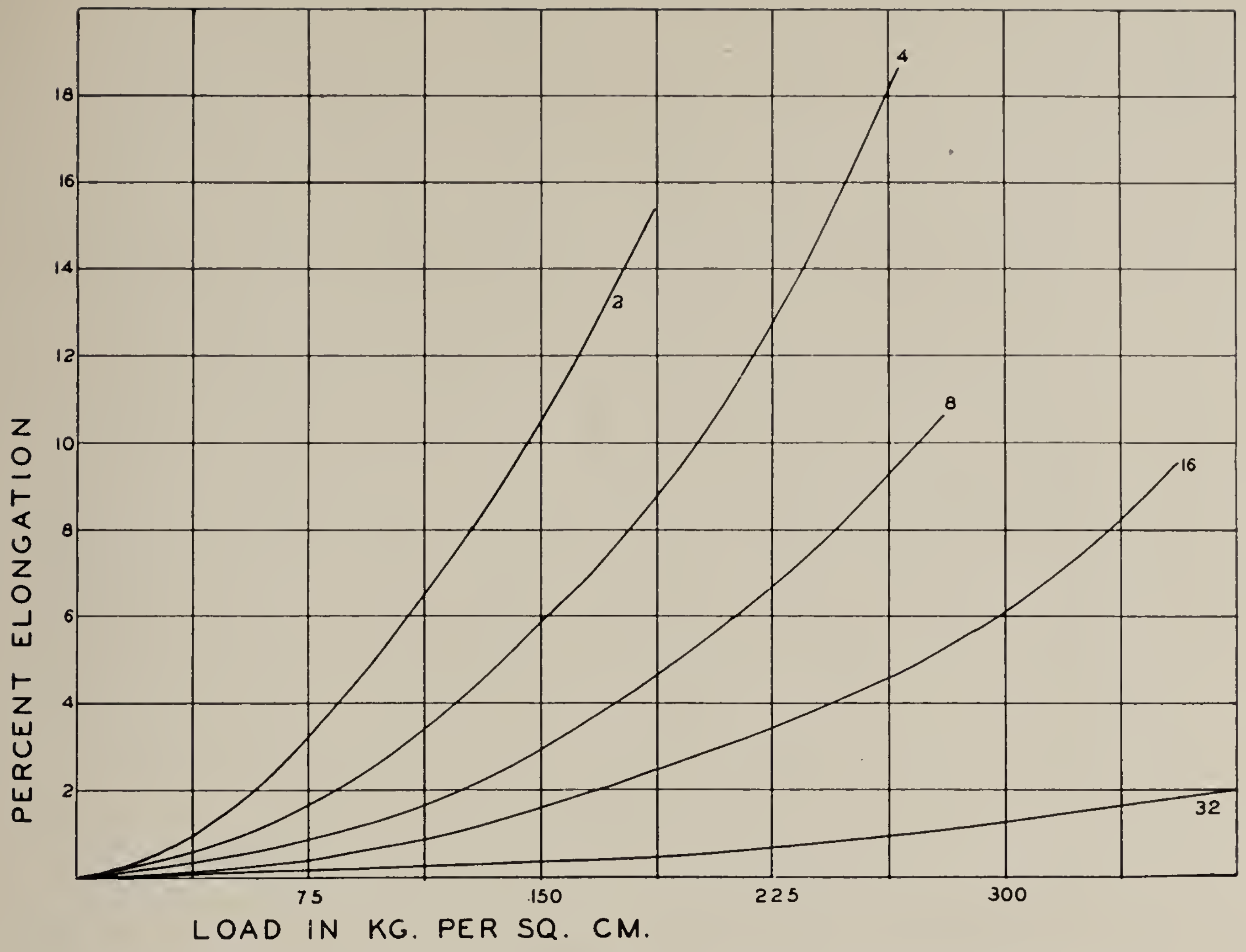

Fig. XI-13. Stress-strain properties of pigmented trilinolein films.

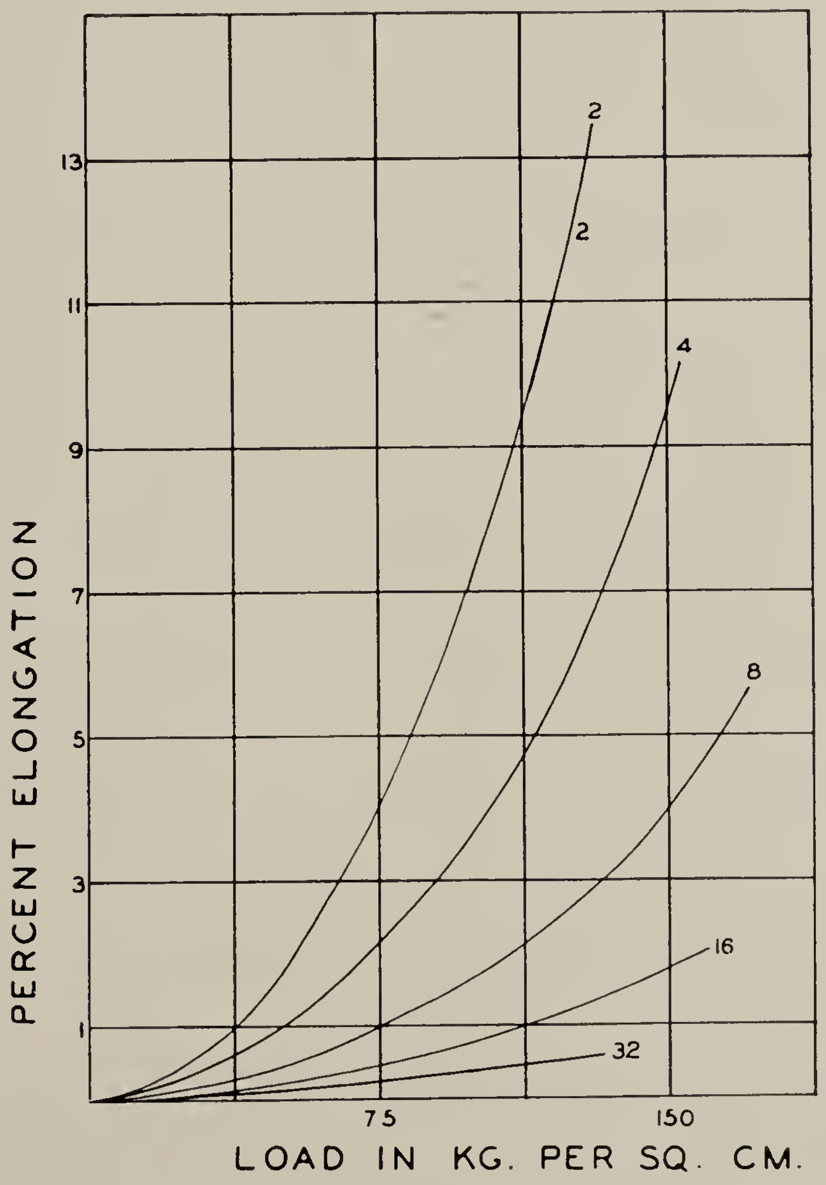

Fig. XI-14. Stress-strain properties of pigmented trilinolenin films.

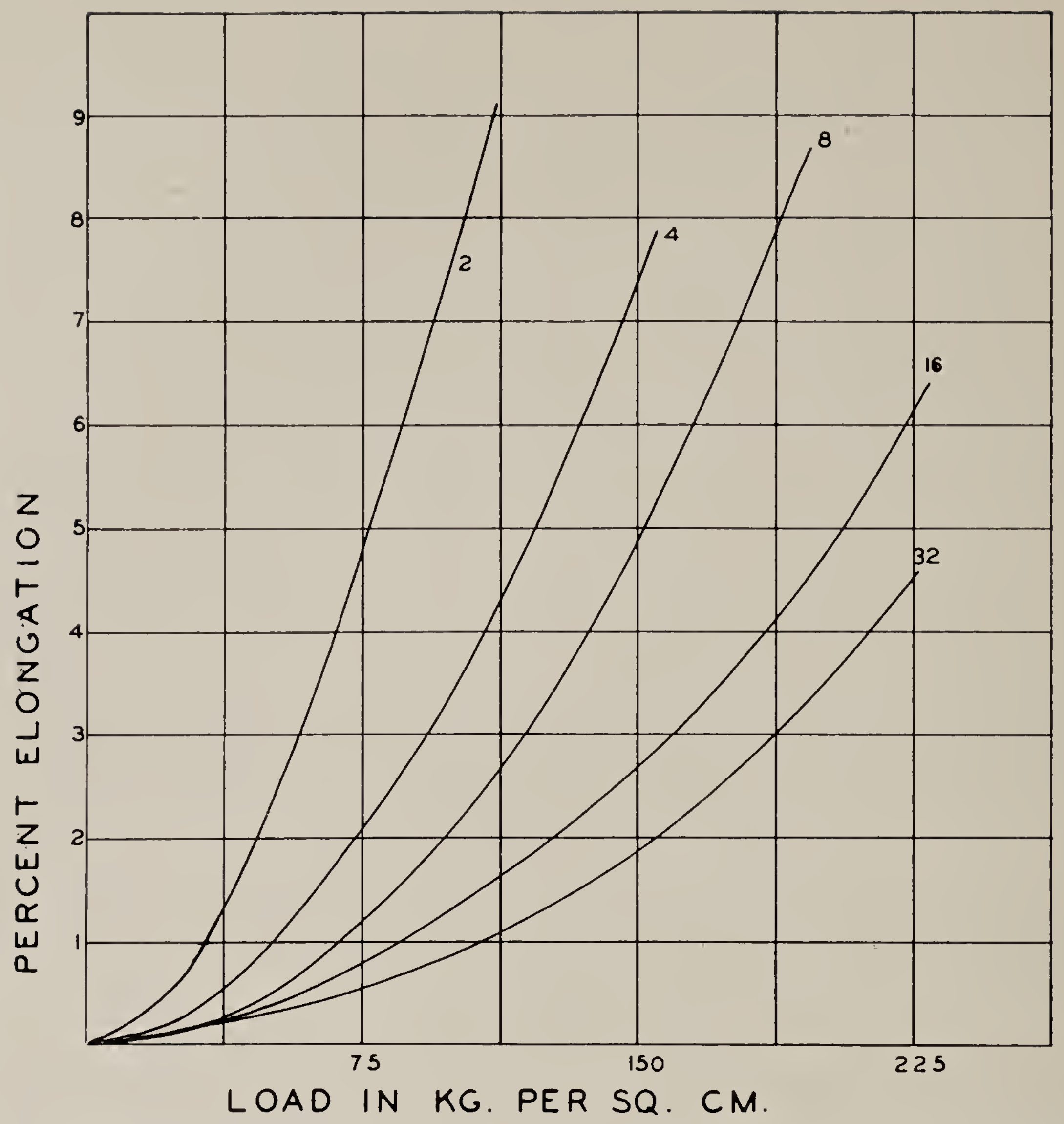

Fig. XI-15. Stress-strain properties of pigmented trieleostearin films.

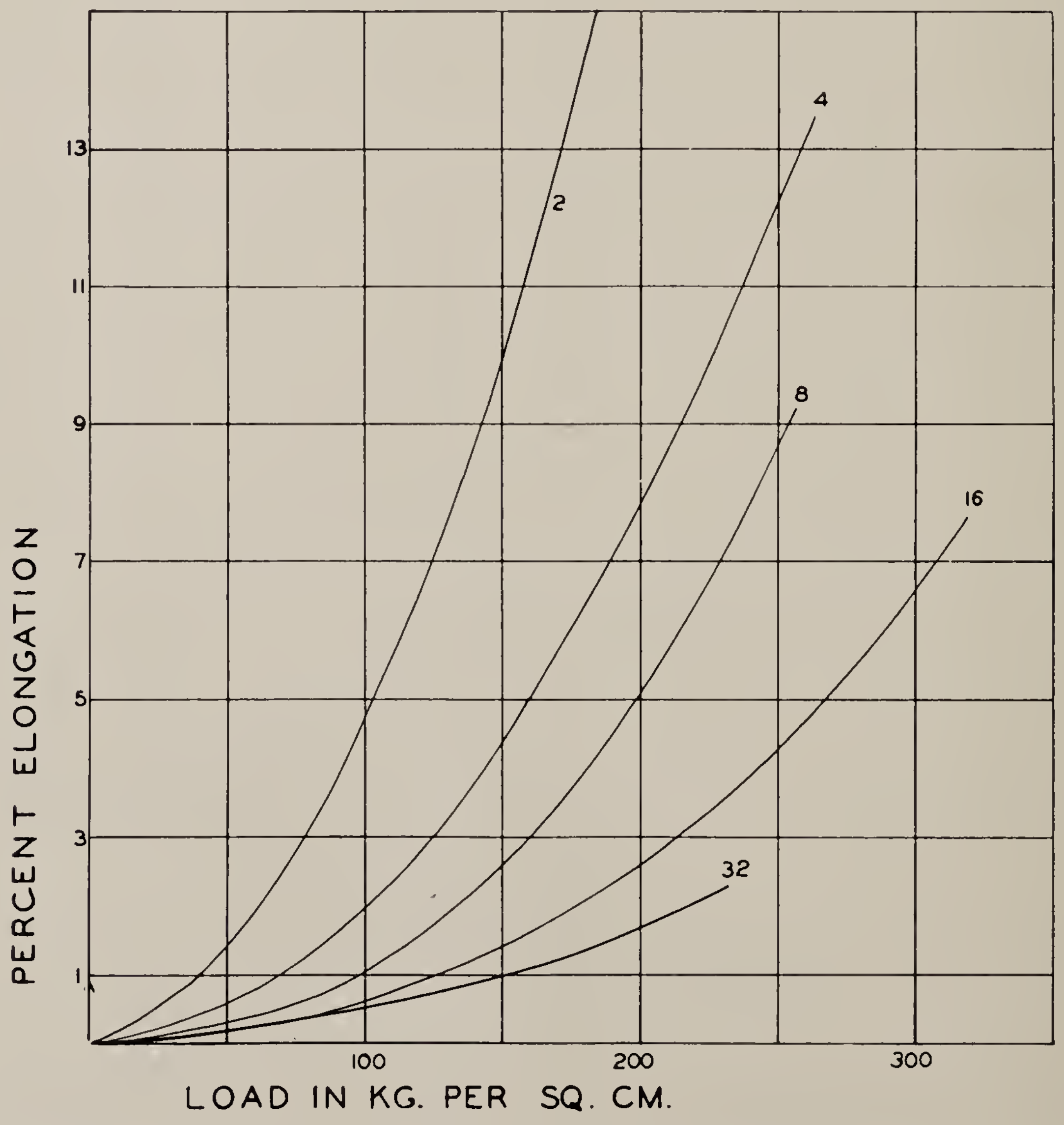

Fig. XI-16. Stress-strain properties of pigmented PE linoleate films.

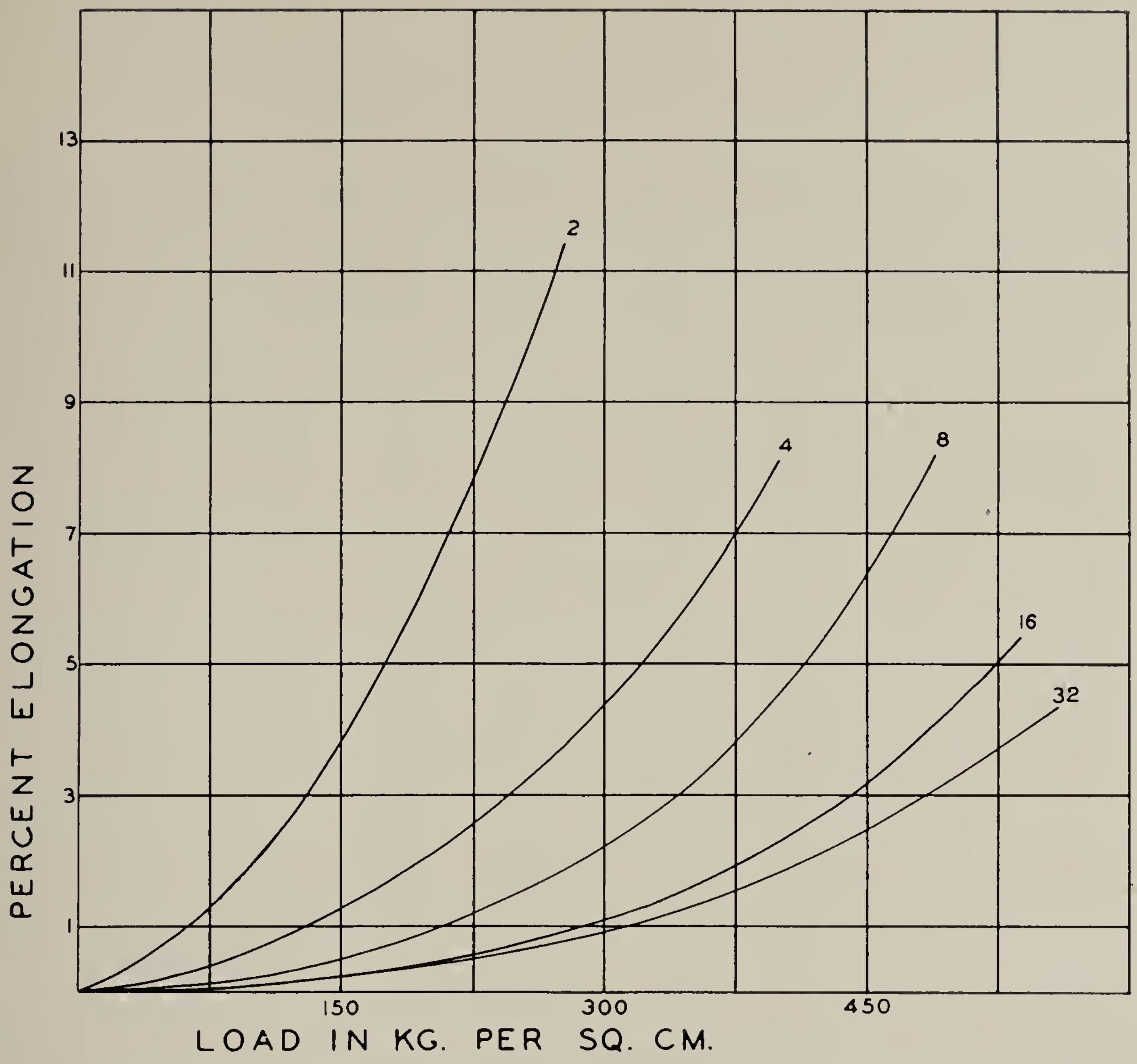

Fig. XI-17. Stress-strain properties of pigmented PE linolenate films.

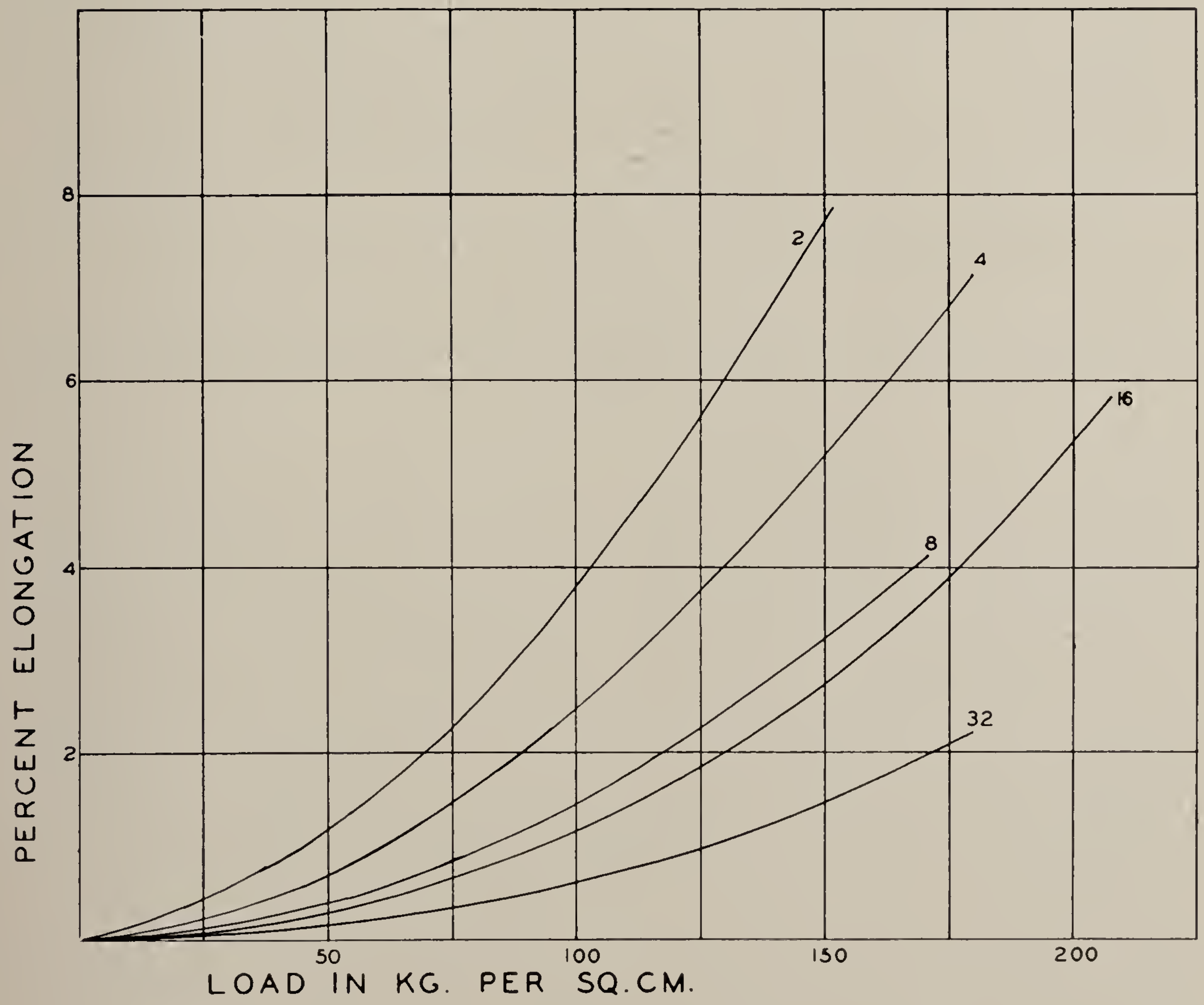

Fig. XI-18. Stress-strain properties of pigmented PE eleostearate films.

able to strict control make the tensile strength of a protective coating material of little practical value. There are so many hazards in preparing a film specimen for a stress-strain analysis that very few tensile values are ever obtained which accurately represent its inherent ultimate strength. Accordingly, many investigators automatically discard all lower values and accept as more nearly correct the highest figure obtained in any one experimental run. Besides, the rate of applying the load seriously affects the breaking strength, and it would be foolish to try to generalize on the basis of a figure obtained under one narrowly limited set of experimental conditions. Dr. Elm confined his discussión, therefore, to the possible interpretation of the significance of the shape of the stress-strain curves.

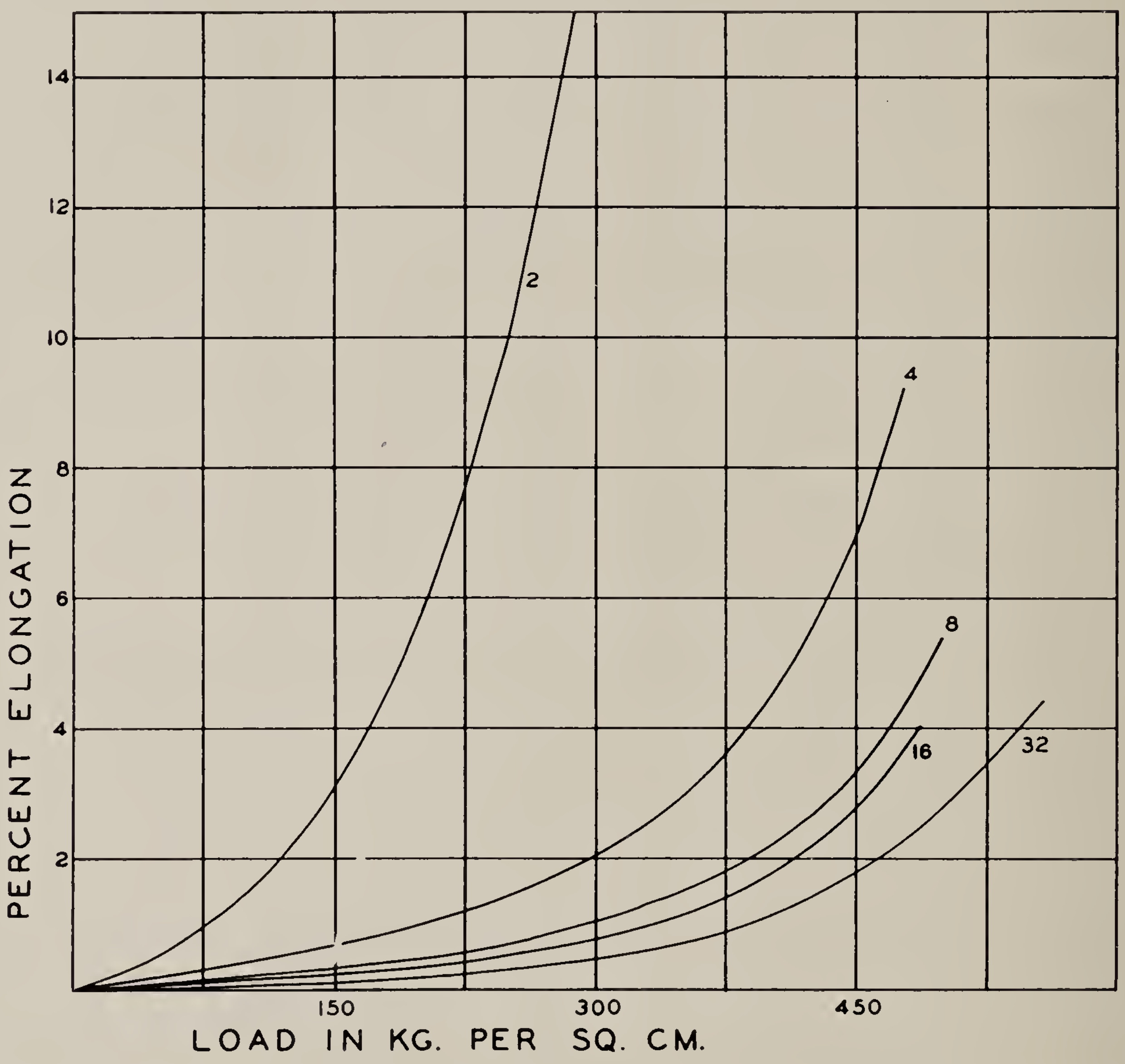

Fig. XI-19. Stress-strain properties of pigmented LO linoleic glycerol alkyd films.

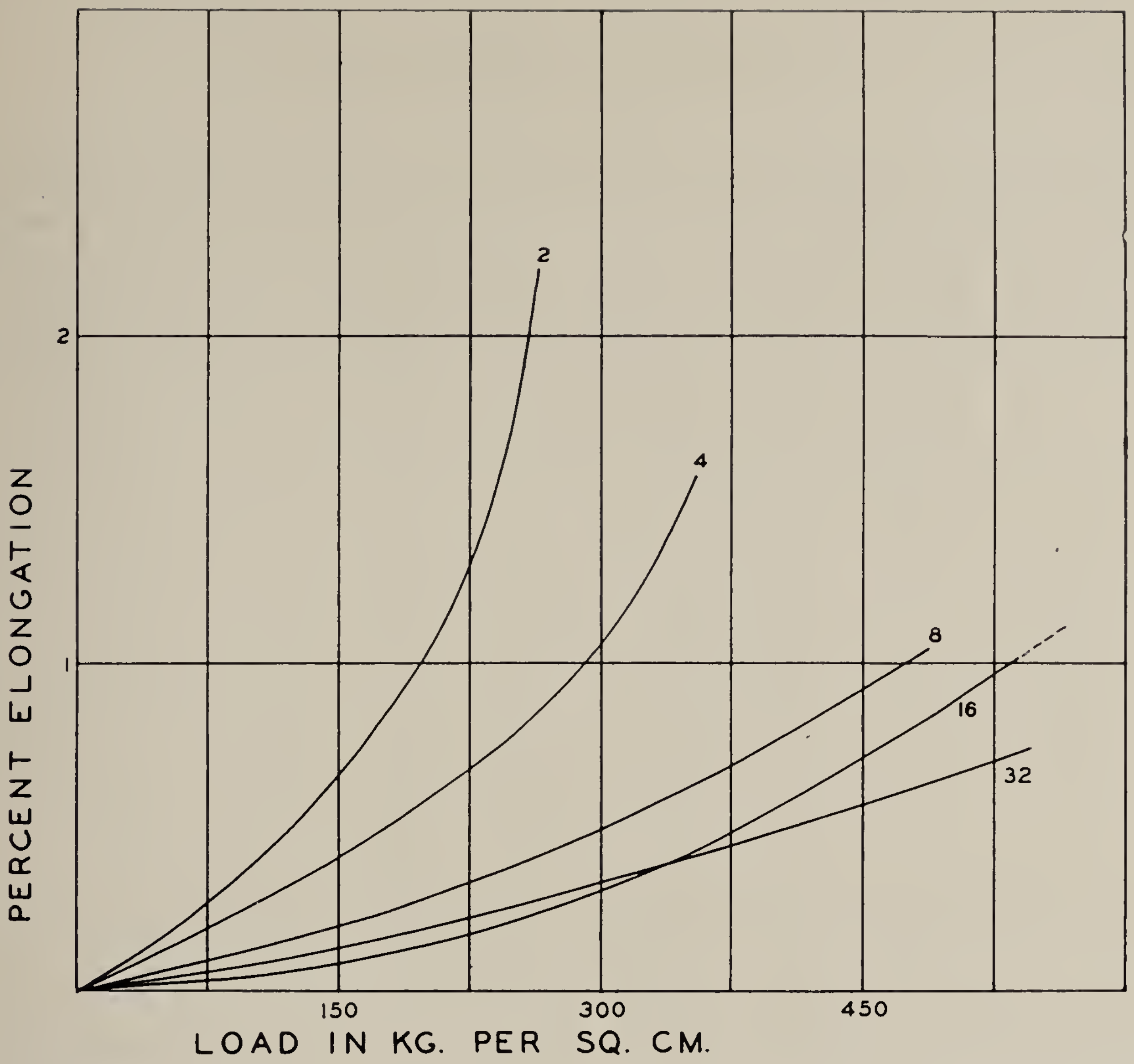

Fig. XI-20. Stress-strain properties of pigmented LO linolenic glycerol alkyd films.

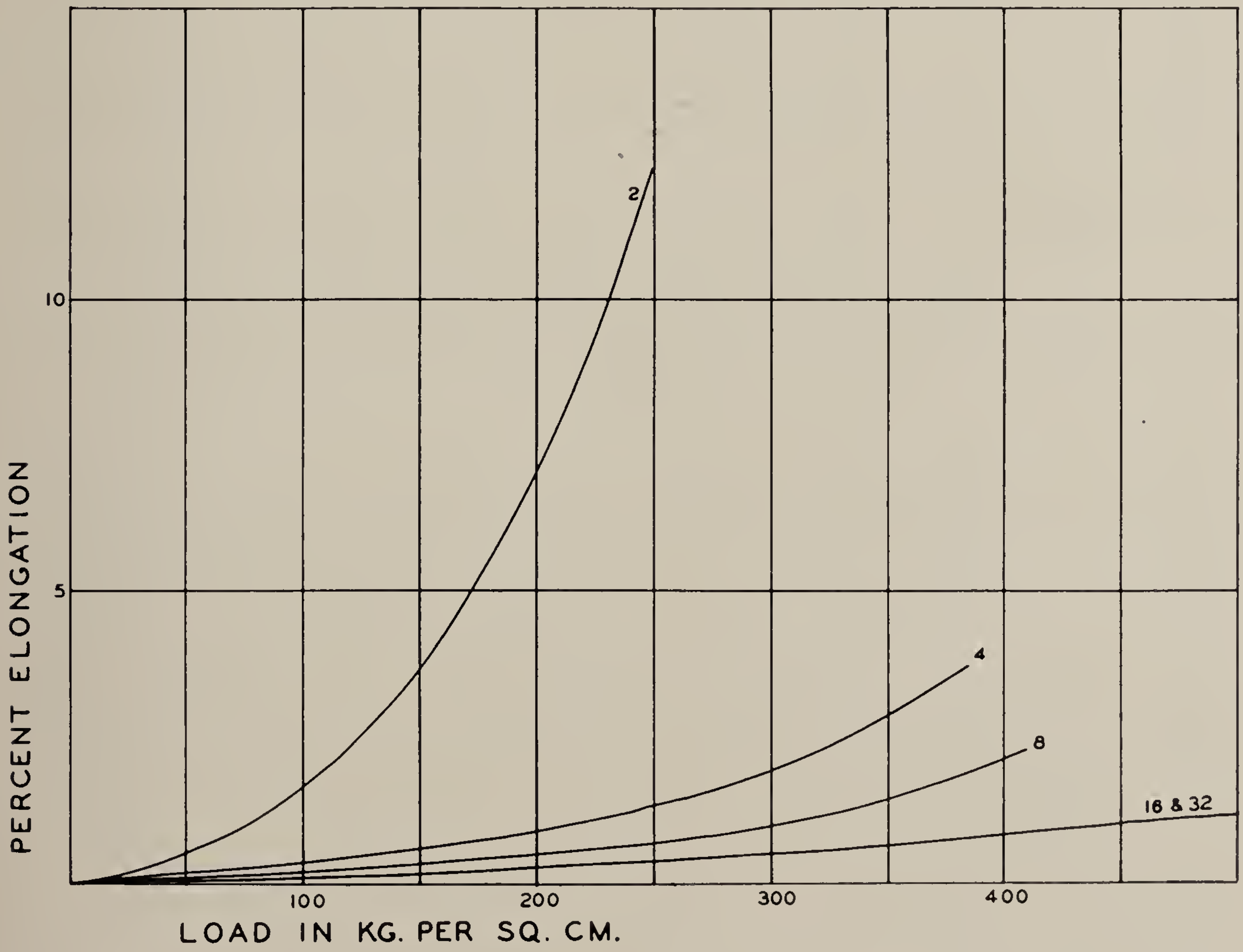

Fig. XI-21. Stress-strain properties of pigmented SO linoleic glycerol alkyd films.

A difficulty frequently encountered in distensibility studies of organic coating films crops up in the curves for the clear vehicles. Those for the alkyd resins show a gradual and rather consistent change in shape with age, but this consistency is entirely lacking in those for the esters. Apparently the drying and aging schedules under the standardized conditions were quite adequate to produce films of the alkyds rigid enough for stress-strain evaluation, but not of the esters, which were still too soft for that purpose. Pigmentation overcame this difficulty, and all the pigmented specimens yielded curves which can be readily interpreted. The clear eleostearate films wrinkled so badly that thickness could not be accurately measured; hence comparisons of their stress-strain results with other compounds are impossible.

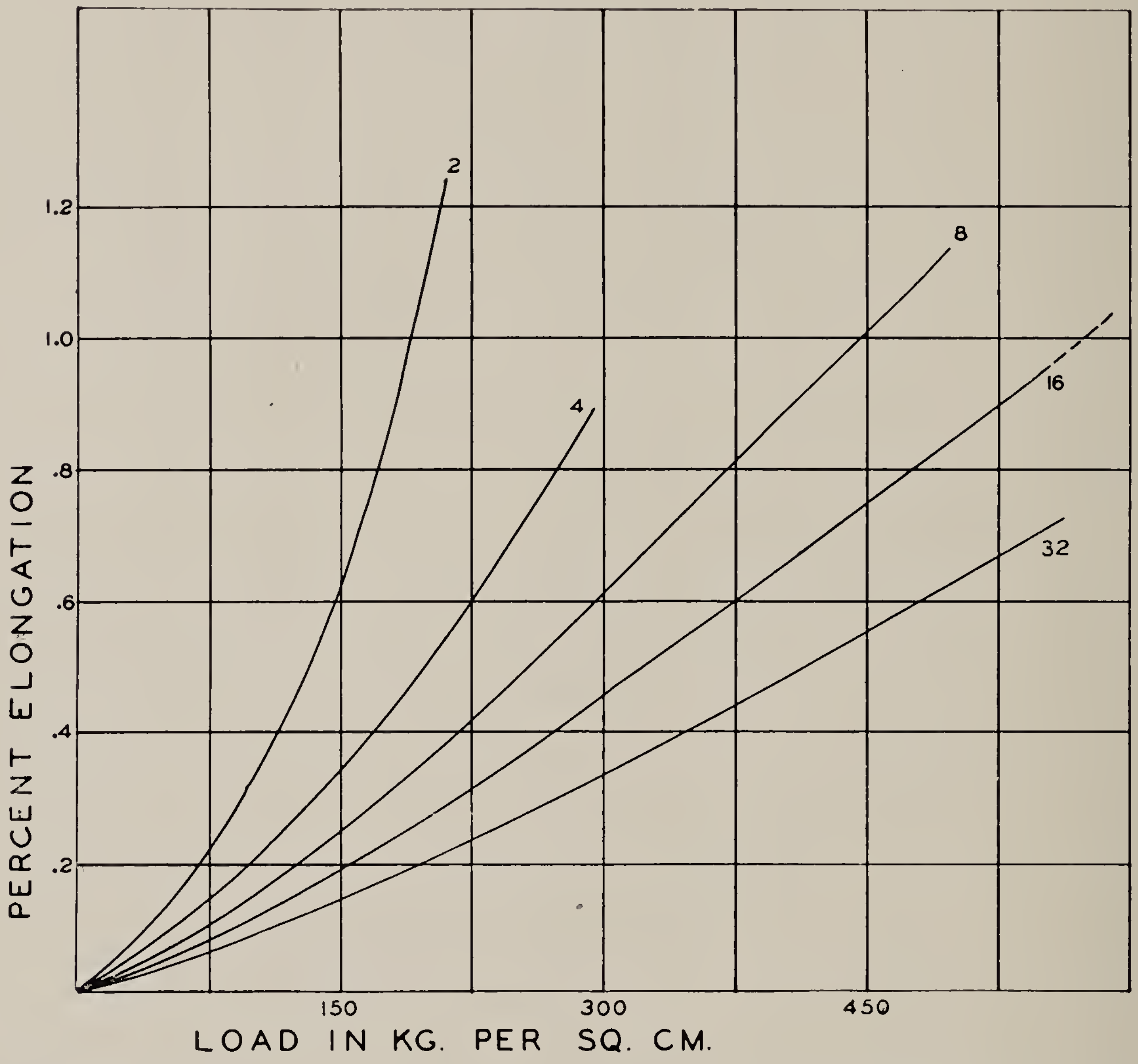

Fig. XI-22. Stress-strain properties of pigmented SO linolenic glycerol alkyd films.

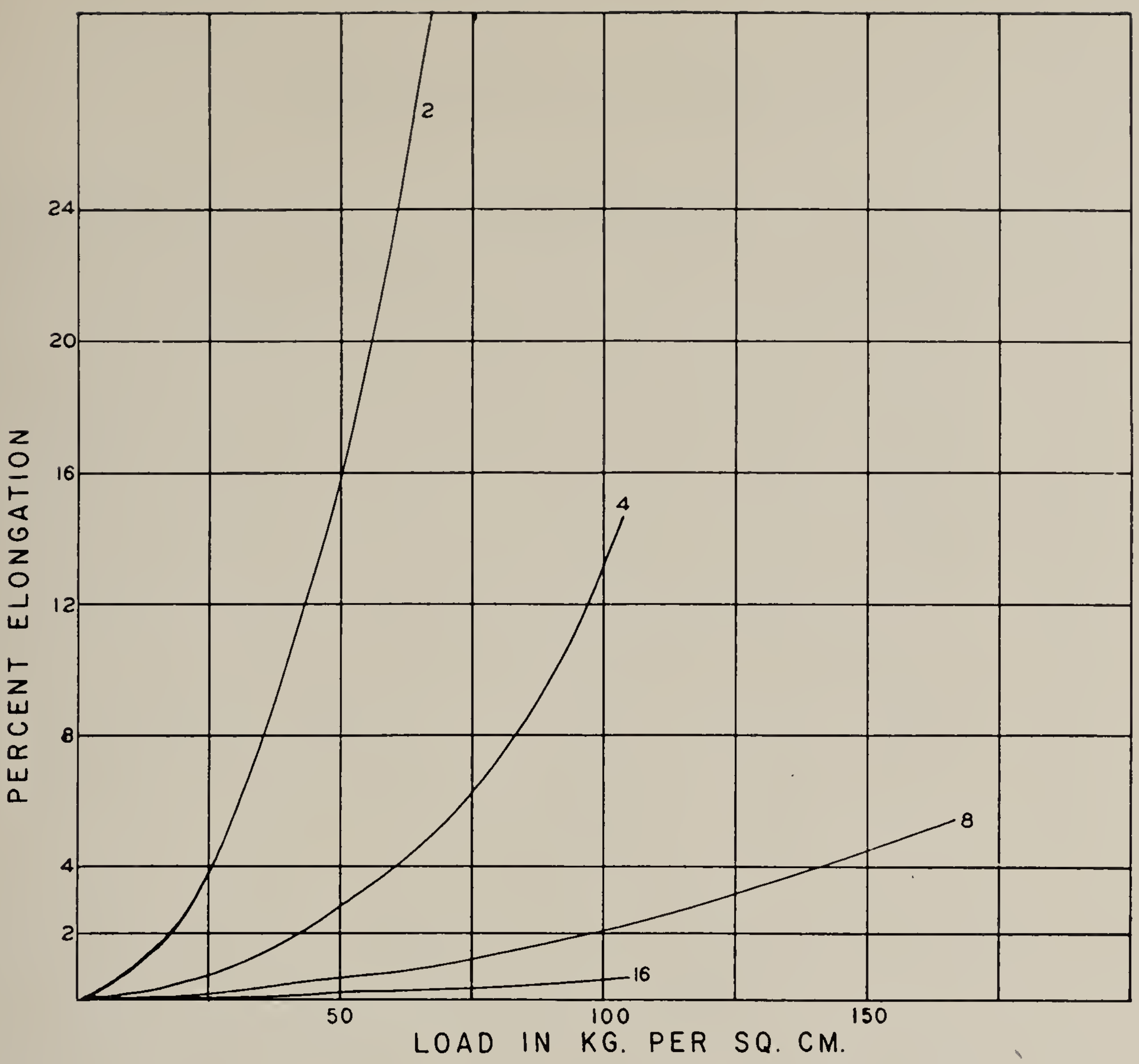

Fig. XI-23. Stress-strain properties of pigmented varnish linseed oil films.

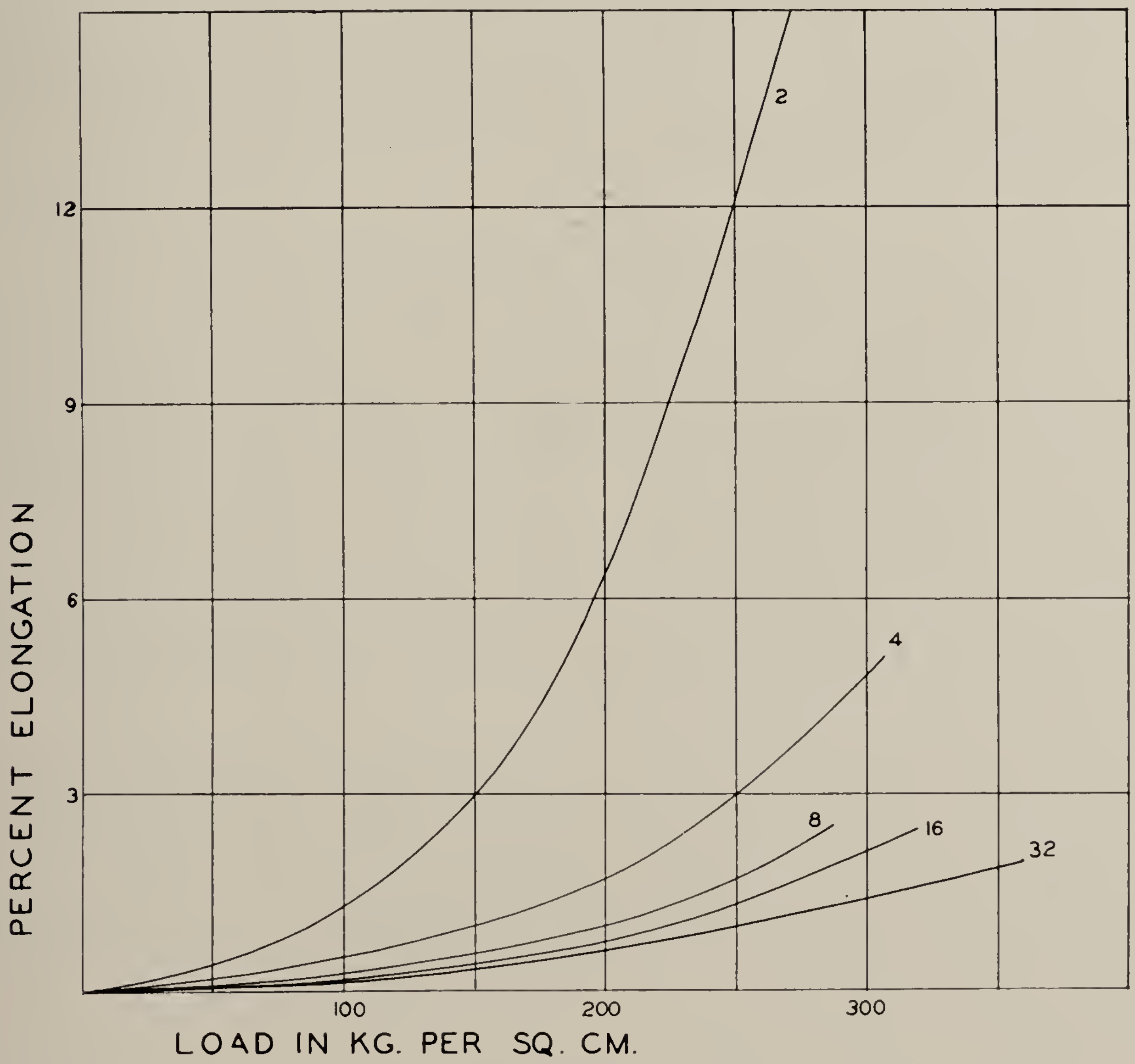

Fig. XI-24. Stress-strain properties of pigmented commercial alkyd films.

To convey a more practical meaning for the paint technologist, the load-elongation curves must be converted to some numerical value of distensibility. Dr. Elm felt that the best way to do this was to measure the area under each stress-strain curve. Since the load at point of rupture (the tensile strength) varied considerably, he selected a standard load value (that of the shortest abscissa) in each set of curves, in order to guarantee distensibility figures which could be compared with each other. This corresponded with the load at rupture for the youngest of the specimens tested. This standard load value was different for each vehicle, but it gave directly comparable distensibility values for all the specimens of any one material. The property which he felt to be of greatest interest was not the absolute distensibility of any vehicle but its susceptibility to change under the standard conditions of aging.

The areas in square inches, measured by a planimeter, were converted to load times elongation, or distensibility, units by multiplying by the load times elongation units per square inch for each individual chart. Though the distensibility values obtained were still arbitrary, they were more representative of the relative distensibility properties of the various vehicles and paints than the square inch areas obtained by the planimeter. They are shown for the clear films in Table XI-1 and for the pigmented ones in Table XI-2, at aging periods up to 52 weeks.

TABLE XI-1

Changes on Aging in Relative Distensibility of Clear Alkyd Films

	Age in weeks					
Material	2	4	8	16	32	52
LO linoleic glycerol alkyd	4447	2610	1540	653	513	197
LO linolenic glycerol alkyd	1083	600	287	257	123	*
SO linoleic glycerol alkyd	3330	*	2087	593	543	190
SO linolenic glycerol alkyd	912	378	140	128	96	*
Commercial alkyd	5380	4107	2740	2277	*	963

* No measurements made owing to difficulties with the particular specimens, the apparatus, or the experimental controls.

Upon examining these data, one might be tempted to compare distensibilities of the various compounds; but Dr. Elm warned again that although such a comparison might be correct, it is not justified in view of the way the figures were obtained, and that it is permissi-

TABLE XI-2

Changes on Aging in Relative Distensibility of Films of Pigmented Compounds

Material	Age in weeks 2	4	8	16
Trilinolein	1740	940	514	272
Trilinolenin	873	446	201	93
Trieleostearin	816	395	239	143
PE linoleate	1213	527	317	179
PE linolenate	2610	894	437	225
PE eleostearate	977	650	398	329
LO linoleic glycerol alkyd	1460	245	117	98
LO linolenic glycerol alkyd	282	132	66	33
SO linoleic glycerol alkyd	1697	227	122	64
SO linolenic glycerol alkyd	251	114	79	60
Varnish linseed oil	922	153	46	11
Commercial alkyd	1605	445	250	185

ble to compare only the rates of loss of distensibility. This is done graphically in Fig. XI-25 for the clear alkyd films, where distensibility is plotted against weeks of aging on a logarithmic scale. Whether any particular curve is located higher or lower in this coordinate system than any other curve has no practical meaning. Significance attaches solely to the slopes of the curves, which indicate the rate at which distensibility is lost and thus the rate of embrittlement and of increasing likelihood of failure by mechanical disintegration.

Perhaps straight lines through the points shown are not the most accurate "curves" to represent the relationships. But in view of the really tremendous experimental difficulties of establishing and maintaining complete control over all variables at all times, straight lines are probably best because they bring out clearly the general trend of the effect of age on distensibility.

The almost identical slope of the lines *A, B, C,* and *D* means, most importantly, that the four synthetic alkyds age at about the same rate, without regard to length or to type of modifying acid (linoleic or linolenic). The commercial alkyd used as a control aged a little more slowly, suggesting that its modifying acid differs in some essential way from those commonly found in linseed oil.

The effect of pigmentation upon distensibility as a measure of aging rate is shown in Fig. XI-26. This effect is clearly seen to be insignificant, in a matrix of the type here studied and under the chosen conditions. One may be surprised at this in view of the known influence of pigments upon the weathering properties and failure of paints. Yet this inconsistency may be only apparent; the rate of aging, it seems, is a function of the film matrix, but the outward manifestations of the aging process may well be dependent upon the pigment imbedded in it.

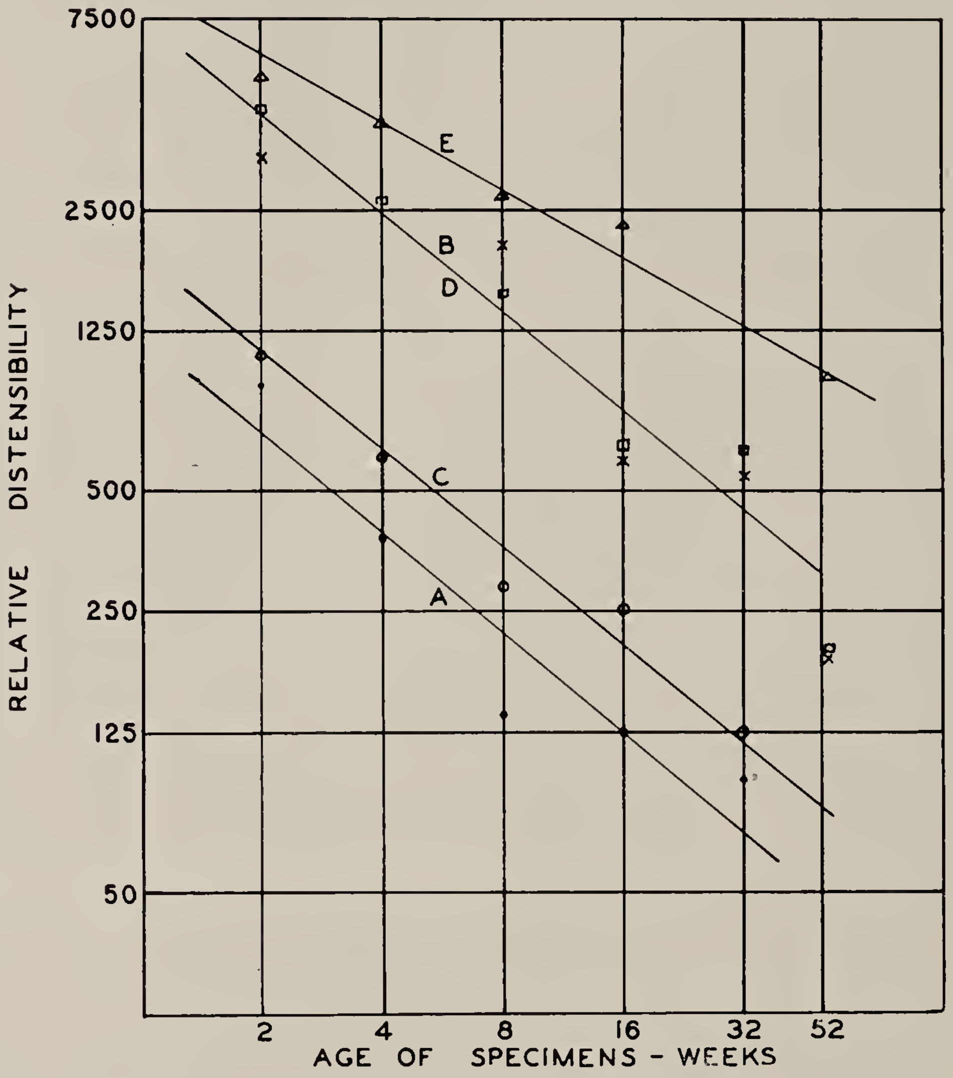

Fig. XI-25. Changes in distensibility of clear alkyd films. A, SO linolenic glycerol alkyd; B, SO linoleic glycerol alkyd; C, LO linolenic glycerol alkyd; D, LO linoleic glycerol alkyd; E, commercial alkyd.

A significant observation is brought out by Fig. XI-27. The pigmented ester of eleostearic acid is seen to embrittle at a markedly lower rate than the corresponding film containing linolenic acid. This finding agrees well with practical experience; it is a manifestation of the essential difference between conjugated and nonconjugated media, and it indicates conclusively that these media differ not only in film formation characteristics but also in aging properties.

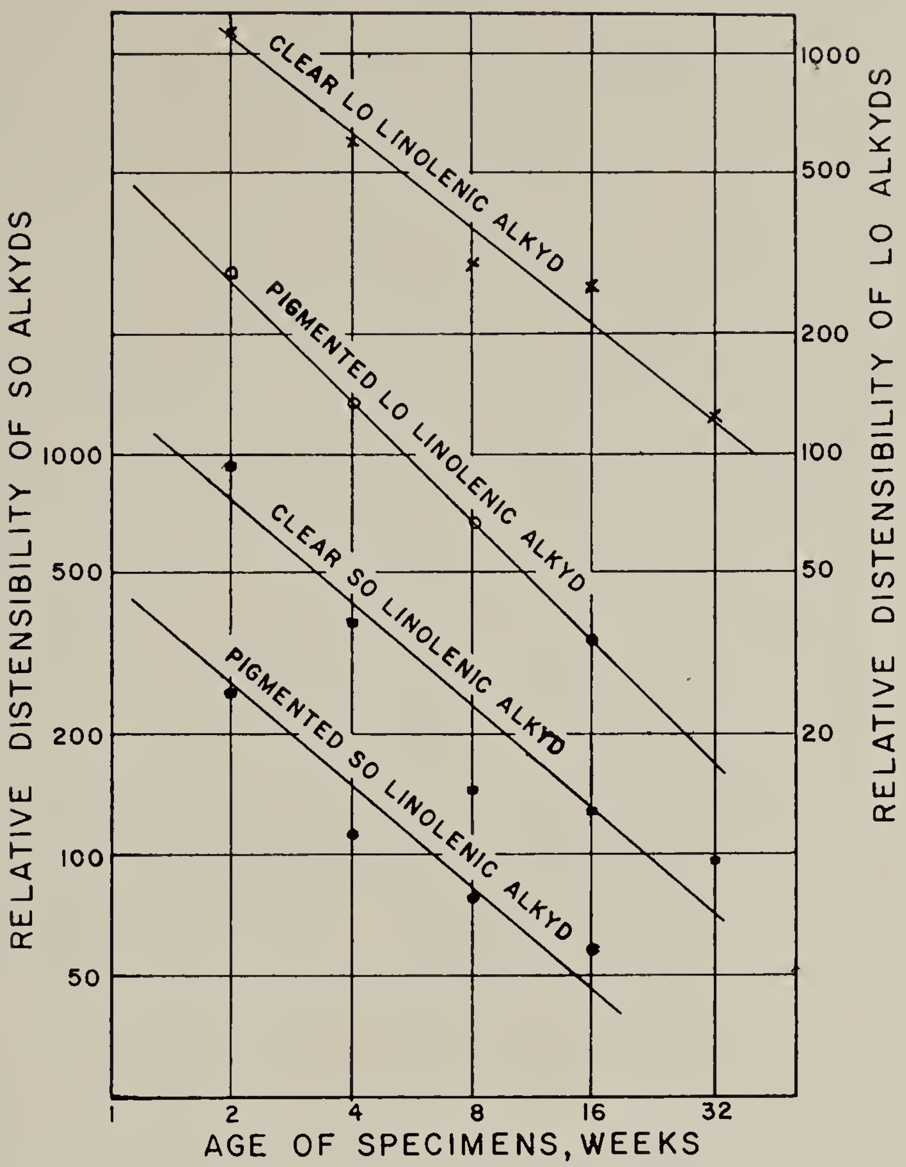

Fig. XI-26. Effect of pigmentation on distensibility changes.

Figure XI-28 presents a comparison of the aging properties of the paints made from the two commercial materials tested in this project. The slower aging rate of the commercial alkyd, as compared with varnish linseed oil, may possibly be due to a content of conjugated material.

Dr. E. B. FitzGerald, in evaluating Elm's work, questioned the validity of comparisons of aging rate when the maximum tensions used in calculating distensibility varied from one material to another. Taking the equation

$$P_i = f(s) \text{ at constant age} \qquad (1)$$

where P_i is per cent elongation of substance i, and s is load in kilograms per square centimeter, then

$$D_i = \int_{s=0}^{s=Z} P_i ds \qquad (2)$$

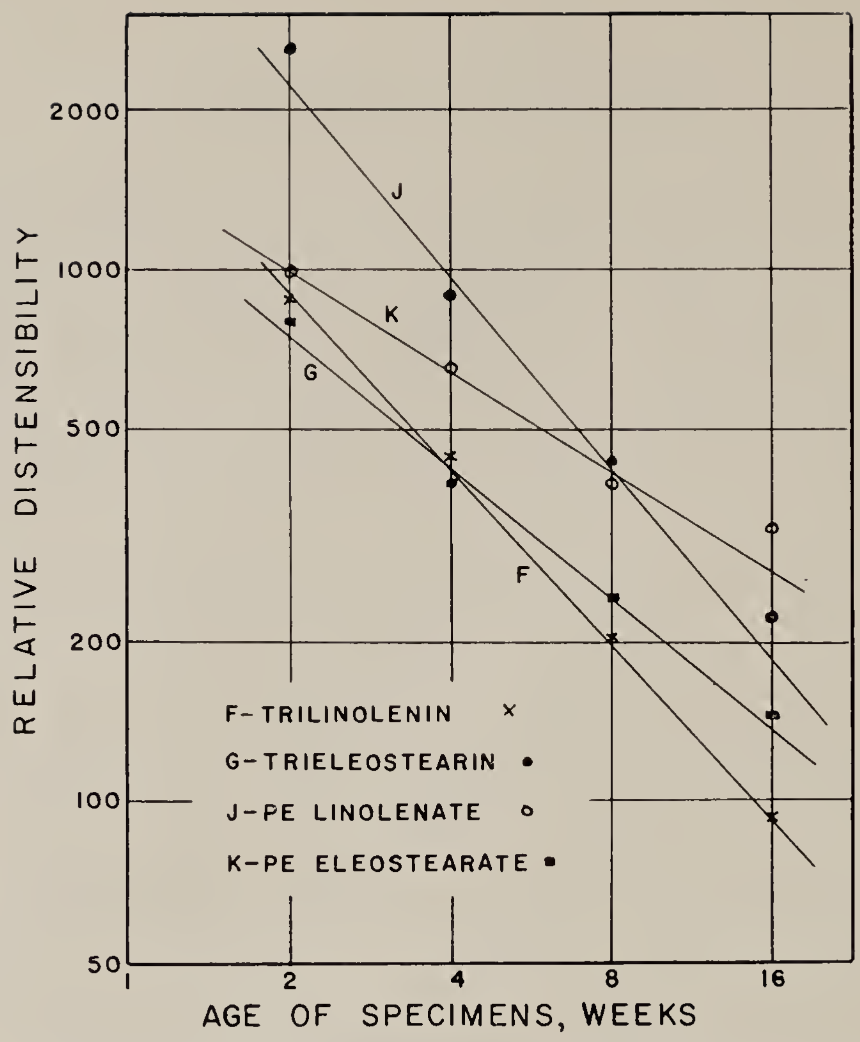

Fig. XI-27. Effect of conjugation on distensibility changes.

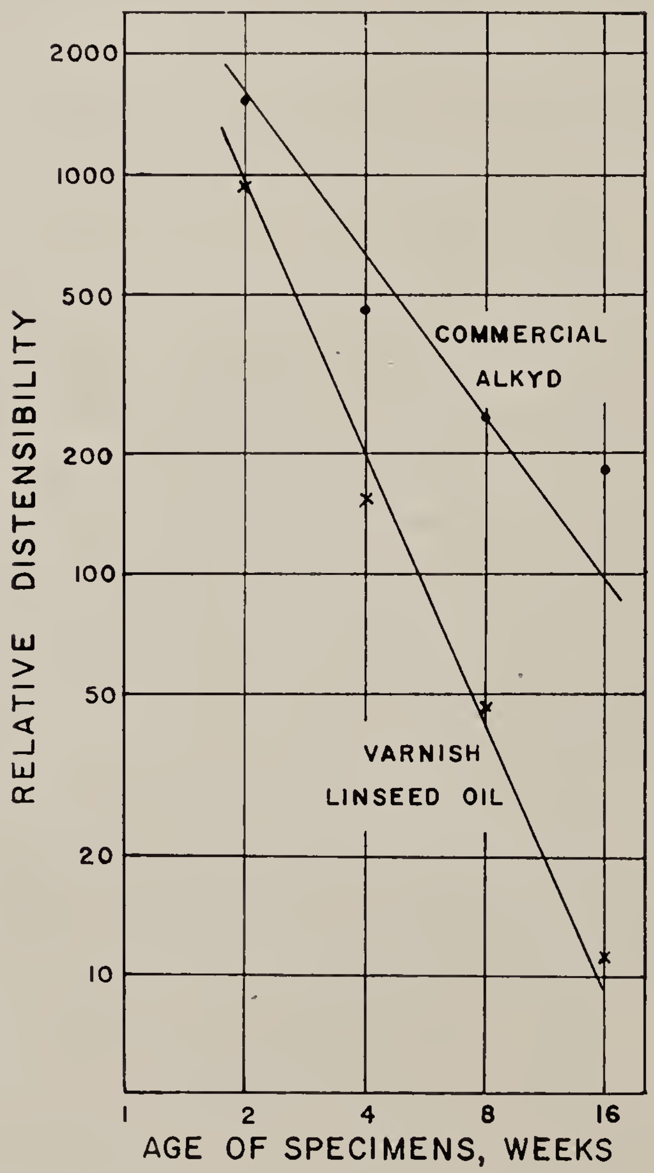

Fig. XI-28. Changes in distensibility of pigmented commercial vehicles.

where Z is an arbitrarily chosen value of the load. The assumption is made that values of distensibility, D_i, calculated in this way for several values of age and a single value of Z, may be represented by the equation:

$$D_i = ma^{\mu} \tag{3}$$

where a is age and μ is a constant which is characteristic of the change experienced by a given material on aging. It is further assumed that values of μ so obtained are independent of Z, so that μ_i may be compared with μ_j even though, for experimental reasons, different values of Z were used in the separate calculations of D_i and D_j.

In view of these considerations, data which Elm presents graphically may be summarized numerically by listing the characteristic values of μ for each material. These may be obtained graphically (μ_g) by measuring the slopes of Elm's log D versus log a plots, or they may be calculated (μ_c) from his tabulation of D versus a. For the latter purpose, use is made of the relation

$$\text{Slope} = \frac{(\Sigma\, x)\ (\Sigma\, y)\ -\ n\ (\Sigma\, xy)}{(\Sigma\, x)^2 - n\ (\Sigma\, x^2)} \tag{4}$$

in which $x = \log D$ and $y = \log a$. Differences between μ's obtained by these two methods should provide an estimate of the error in slope to be expected in striking a straight line through a set of points of imperfect linearity. Results appear in Table XI-3, which also shows the loads (Z) at which the distensibilities were calculated.

By comparing the slopes of the logarithmic distensibility plots, equivalent to μ_g values in Table XI-3, Elm reached the conclusions shown on pages 291 to 293.

An examination of the μ values in this table reveals several interesting facts. Foremost among these are the discrepancies which exist between the values read from the graphs and those calculated from the original tabulated data by means of equation (4). As explained above, this indicates poor linearity in some of the sets of points and the possibility of error due to judgment in striking a straight line through such a set. It may be argued that judgment could be superior to an arbitrary averaging process such as represented by equation (4). Where only a few points are involved, this may be so, but the discrepancies indicate a dependence on judgment rather than on wholly objective measurements.

TABLE XI-3

Relative Susceptibility to Change on Aging

Compound	Clear			Pigmented		
	μ_g	μ_c	Z	μ_g	μ_c	Z
Trilinolein	*	*	*	+	−0.94	238
Trilinolenin	*	*	*	−1.26	−1.05	125
Trieleostearin	*	*	*	−0.92	−0.83	125
PE linoleate	*	*	*	+	−0.94	200
PE linolenate	*	*	*	−1.12	−1.05	250
PE eleostearate	*	*	*	−0.64	−0.50	250
LO linoleic glycerol alkyd	−0.83	−0.93	125	+	−1.27	250
LO linolenic glycerol alkyd	−0.83	−0.80	250	−0.83	−1.00	250
SO linoleic glycerol alkyd	−0.83	−0.85	125	+	−1.44	250
SO linolenic glycerol alkyd	−0.83	−0.82	250	−0.83	−0.67	225
Varnish linseed oil	*	*	*	−2.44	−2.11	62.5
Commercial alkyd	−0.57	−0.57	50	−1.00	−1.05	250

* Stress-strain curves too erratic to permit distensibility calculation.

+ Distensibility tabulated, but not plotted, in Elm's report.

Next, the wide range of loads (Z values) at which distensibilities were calculated suggests that in certain cases the results could depend markedly upon the validity of the assumptions implicit in equations (2) and (3). For example, the conclusion that the clear commercial alkyd ages more slowly than the synthetic alkyds is based on a calculation for the former at 50 kg. per square centimeter and for the latter at 125 to 250 kg. per square centimeter. The finding that the linseed oil paint ages faster than that made from the commercial alkyd depends on distensibilities figured at 62.5 and 250 kg. per square centimeter, respectively. Thus it is important to estimate the extent to which μ is dependent on Z.

For the purposes of this discussion, FitzGerald took original data for the commercial alkyd paint to obtain this relation. He made a photographic enlargement, three times original dimensions, from Elm's graph of elongation versus load as published, and measured distensibilities by planimeter at loads of 150, 200, and 250 kg. per square centimeter (corrected values). Corresponding values of μ were then computed using equation (4), with these results:

Z	μ_c
150	−0.85
200	−0.92
250	−0.95

The small discrepancy between μ_c as found here for $Z = 250$ and that given in Table XI-3 is an indication of the reproducibility of a calculation which involves numerous planimeter measurements. Errors may also have crept in owing to faulty optics or irregular shrinkage of paper in the photographic process, in spite of care taken to minimize them. It thus appears fairly certain that between μ and Z there exists a direct relation which introduces an element of doubt concerning the conclusions just mentioned.

The fact remains, however, that vast differences in mechanical behavior exist between the various materials when compared on an absolute basis. To obtain absolute values of distensibility, according to Elm's definition, at a single load for all would be practically impossible because of the small areas which would have to be accurately measured for the weaker films. These differences may be observed and compared from the stress-strain plots, and an approximate comparison is afforded by reading from these plots the stress needed to stretch the two-week-old specimen of each material by 1%. These values are listed in Table XI-4.

This table is presented in spite of Elm's repeated warnings that variability in experimental conditions makes such comparisons misleading. The principal brief held for this tabulation is that it brings out the tremendously wide range of properties more clearly than the μ values given above.

On the other hand, even conceding an error in these data of ±50%, FitzGerald unhesitatingly concludes that films laid by the synthetic alkyds tested by Elm (which included neither oleic nor eleostearic resins) are an order of magnitude "stiffer" at two weeks of age than those from either the commercial alkyd or simple esters; and that pigmentation invariably produces a large increase in this mechanical property. Since tests of dryness or hardness, either by the finger or instruments, involve deformations in the order of 1%, it seems reasonable to compare the data in Table XI-4 with results relating to these properties from other projects. The only such projects directly related to mechanical behavior were those of Kiser and Coulliette (Chapter VII) on hardness and abrasion resistance, and unfortunately the data on abrasion resistance given by these cooperators were too erratic to permit any conclusions. However, their Sward rocker hardness values reveal a rough correlation in that hardness was invariably found to be greater for pure alkyds than for esters, with the commercial alkyd in intermediate position. Pigmentation, however, did not appear to make any particular difference in hardness, but hardness always increased with age. The comparisons are summarized in Table XI-5.

TABLE XI-4
Approximate Stress at 1% Elongation (kg./cm.^{2})

Compound	Clear		Pigmented	
	2 wk.	16 wk.	2 wk.	16 wk.
Trilinolein	1.5	0.75	37.5	113
Trilinolenin	2.0	2.0	37.5	113
Trieleostearin	0.5	1.0	32.5	87.5
PE linoleate	2.25	1.5	37.5	125
PE linolenate	—	—	62.5	288
PE eleostearate	1.75	3.0	68.8	138
LO linoleic glycerol alkyd	7.5	25	75	325
LO linolenic glycerol alkyd	67.5	150	198	538
SO linoleic glycerol alkyd	32.5	60	85	500
SO linolenic glycerol alkyd	100	213	188	575
Varnish linseed oil	—	—	10	113
Commercial alkyd	2.5	3.0	87.5	210

TABLE XI-5
Comparison of Stiffness and Hardness

Material	Stiffness*				Sward hardness$^+$			
	Clear		Pigmented		Clear		Pigmented	
	2 wk.	16 wk.	2 wk.	16 wk.	1 wk.	12 wk.	1 wk.	12 wk.
Esters	1.5	1.75	37.5	140	2	3	5	7
Pure alkyds	52.5	112.5	137.5	485	17	26	9	28
Commercial alkyd	2.5	3.0	87.5	210	10	11	7	12

* Averaged from Table XI-4.
$^+$ Averaged from Kiser and Coulliette (Chapter VII).

CHAPTER XII

Molecular Size, Shape, and Weight

Trying to measure the size, shape, and weight of individual molecules of the Federation compounds might seem at first glance to be a project of no immediate practical use, even though of fundamental long-range importance. But the technique of getting such information by force-area measurements of monomolecular films proved potentially useful for day-to-day factory control, and the information gained was helpful in explaining the influence of different fatty acids and polyhydric alcohols in these compounds upon the structure and properties of their films.

Lord Rayleigh (22) was an early investigator of monomolecular films. Hardy (9) noticed the orientation of molecules in surface films, and Harkins (11) and Langmuir (15) and their coworkers began a long series of revealing studies of the structure of monomolecular layers. Many other researchers have worked in this field. Biochemists have learned much in it.

Most common of the several techniques for investigating thin surface films on water is the measurement of surface areas of monolayers in relation to applied pressure, using a film balance such as was introduced by Langmuir (16). Long and his coworkers (20) and other investigators improved and modified the instrument, but the present-day hydrophil balances employ the same basic principles as the early models.

In general, water-insoluble materials containing both polar and nonpolar groups, like the Federation vehicles, form monomolecular layers on water; nonpolar liquids (e.g., hydrocarbons) do not. There are exceptions to this rule; some nonpolar liquids yield monomolecular films, some polar ones do not.

Although monolayers are treated as two-dimensional systems, they exhibit a range of phases similar to the gas, liquid, and solid states of three-dimensional systems. Actually five different states are recognizable in many monolayers; they are designated as gaseous, liquid expanded, intermediate, liquid condensed, and solid (10).

Equations of state analogous to those for three-dimensional systems may be applied to some of these. Thus in the gaseous state the equation $FA = KT$ is used, where F is the force in dynes per centimeter, A is the area in square centimeters, K is a constant, and T is the absolute temperature. This corresponds to $PV = KT$, the well-known equation for three-dimensional gases. In the liquid-expanded state, film behavior follows the equation $F(A - b) = KTx$, where b and x are additional factors relating to the cross-sectional areas of the head groups of the molecules and to the forces of attraction between molecules, respectively.

As monomolecular films on water are compressed in the hydrophil balance, a point is reached where the molecules are so close together that further pressure causes a crumpling of the film, shown by a break in the force-area curve. The area of the film at the crumpling pressure may be taken as a measure of the cross-sectional area of the individual molecules. This is not an absolute measure, but for the purposes of the Federation study it served reliably in comparing the areas of the various compounds.

Size, Shape, and Weight of Molecules of Federation Compounds, Project 16—Louisville Club

With a fellowship grant from the Federation, W. R. Lawton carried out this project at the University of Louisville under Dr. Long's direction. Their report appeared in the *Official Digest,* No. 311, 1006 (December, 1950). This chapter contains some data from Lawton's 288-page thesis (19), submitted for his M.S. degree, in addition to what was given in that report.

In order to calculate the number of molecules in a particular film sample, it is necessary to know the molecular weight of the compound under study. Accordingly, the project involved two types of measurement: (*1*) force-area determinations on monomolecular layers on water, using a Cenco hydrophil balance; and (*2*) determination of molecular weights by the common freezing-point-depression method, using cyclohexanol as the solvent.

An illustration of the balance is given in Figure XII-1. The tray, 14 cm. wide, contained water on which the film was established. A

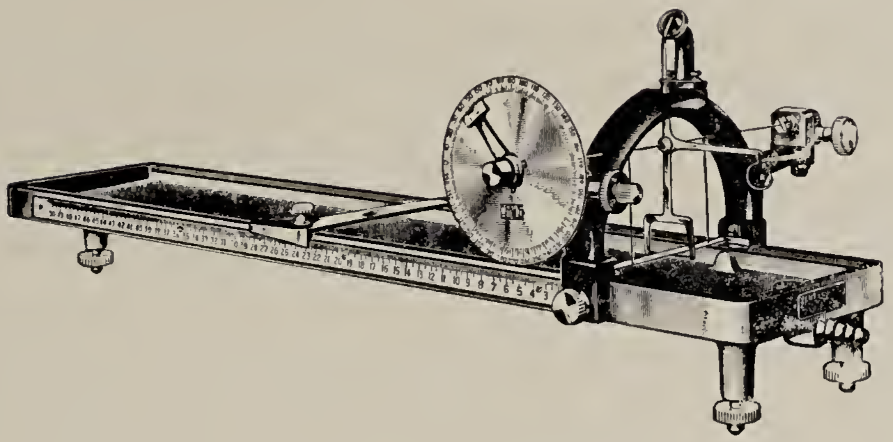

Fig. XII-1. Cenco hydrophil balance.

movable barrier compressed the film, stepwise, against a mica float at the nearer end of the tray. This float was free to respond to pressure on the film but was attached to the sides of the tray by flexible strips of platinum foil so that none of the film could pass around its ends. A torsion wire attached to the float, with a graduated scale adjustment, measured the pressure transmitted to the float by the film. After a monomolecular film had been formed on the water surface, the barrier was moved along a scale from which the film area was determined, and force exerted against the float was read from the torsion scale in relation to that area.

Several factors which affect the behavior of monolayers on water were taken into account in so far as possible in these experiments: (*1*) pH of the water, (*2*) concentration of metallic ions in the water, (*3*) temperature, (*4*) nature of solvent, if any, used in spreading monolayer, (*5*) formation of complexes between compound and water, (*6*) molecular rearrangements produced in some compounds by the compression, and (*7*) rate of compression.

Experimental

Force-Area Determinations

About 0.25 gram of compound was accurately weighed into a 250-ml. volumetric flask, which was then filled to the mark with a c.p. grade of benzene which had been fractionally distilled under vacuum. Films were prepared from this solution as soon as possible; in no case were data reported on solutions more than 3 hours old.

Molten paraffin was brushed on the edges of the tray of the hydrophil balance and on the leading edge of the movable barrier. A benzene solution of paraffin was sprayed on the leading edge of the mica float and the platinum strips.* The torsion scale was calibrated, the tray filled with distilled water, and the surface of the water swept with filter paper. The surface was considered clean when no force was exerted against the float when the barrier was moved as near the float as possible.

The benzene solution of the compound was introduced dropwise here and there on the water surface from a measuring pipet until a slight pressure was registered against the float, and the readings on the torsion scale, begun immediately, were recorded for each 1 cm. forward movement of the barrier, until the latter was within 5 cm. of the float. The time interval between readings was kept as constant as possible; a complete run took about 3 to 4 minutes. Duplicate or triplicate runs were made for all the compounds, and in all cases agreement between runs was close.

For check purposes, a few runs were made on pure samples of oleic, linoleic, and linolenic acids. The results agreed well with previously reported measurements on these materials. In addition to readings on all the Federation vehicles in their original state, a few measurements were made on trilinolein after 45 minutes exposure to air in the hydrophil balance, on trilinolenin after 15 and 60 minutes exposure, and on PE linoleate after 40 and 90 minutes exposure.

Molecular Weight Determinations

The cryoscopic method of Wilson and Heron (24) was employed. The solvents that were present in the alkyds were first removed by evaporation at 80° C. or less under a reduced pressure of 1 mm. of mercury. All materials were then dissolved in cyclohexanol that had been purified by fractional distillation at reduced pressure. Cyclohexanol was an easy choice over other solvents because of its relatively large molecular freezing point depression and its strong solvency for most oleaginous materials.

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* Dr. Long later recognized that this paraffin coating might be partially dissolved by the benzene solution of the compound being studied, leading to erroneous results. In the fall of 1956, after he had joined the faculty of the University of Louisville, he instituted new film-balance studies in which the float and platinum strips were coated with an epoxy-resin varnish, highly resistant to benzene. At the time of going to press these studies were incomplete, but preliminary results for some of the compounds differed significantly from those here given. For final conclusions it will be well to await publication of this new report.

The cyclohexanol solutions were introduced into capillary melting point tubes and the capillaries sealed at both ends. Several tubes were prepared for each compound. The melting points of the pure cyclohexanol and of the solutions were obtained by conventional procedures.

Molecular weights were not determined for most of the esters; chemical analyses had already indicated that they would agree with theoretical values. However, as a check on the method, determinations were made on trilinolein, trilinolenin, and trieleostearin.

Results

Molecular weights as found are recorded in Table XII-1. The observed values for the esters agree well with theory except for trieleostearin, which is about 10% high, suggesting that some polymerization had occurred.

TABLE XII-1
Molecular Weights

	Mol. wt. found
Esters	
Trilinolein	912
Trilinolenin	935
Trieleostearin	972
Alkyds	
LO linoleic glycerol	2445
LO linolenic glycerol	2618
LO eleostearic glycerol	3055
SO linoleic glycerol	4694
SO linolenic glycerol	5028
LO oleic PE	3322
LO linoleic PE	3487
LO linolenic PE	3618
SO oleic PE	10275

Molecular weights of the alkyds are of course considerably higher than those of the esters. From them may be calculated (by multiplying by the oil length percentage and dividing by the molecular weight of the respective glyceryl or PE phthalate) the number of phthalic residues or "bridges" per molecule. These varied from 4.7

for the LO linoleic glycerol alkyd to 11.8 for the SO oleic PE alkyd. The variations are in line, qualitatively, with the relative quantities of the several structural units from which the compounds were synthesized.

Force-area curves for the simple esters are shown in Fig. XII-2

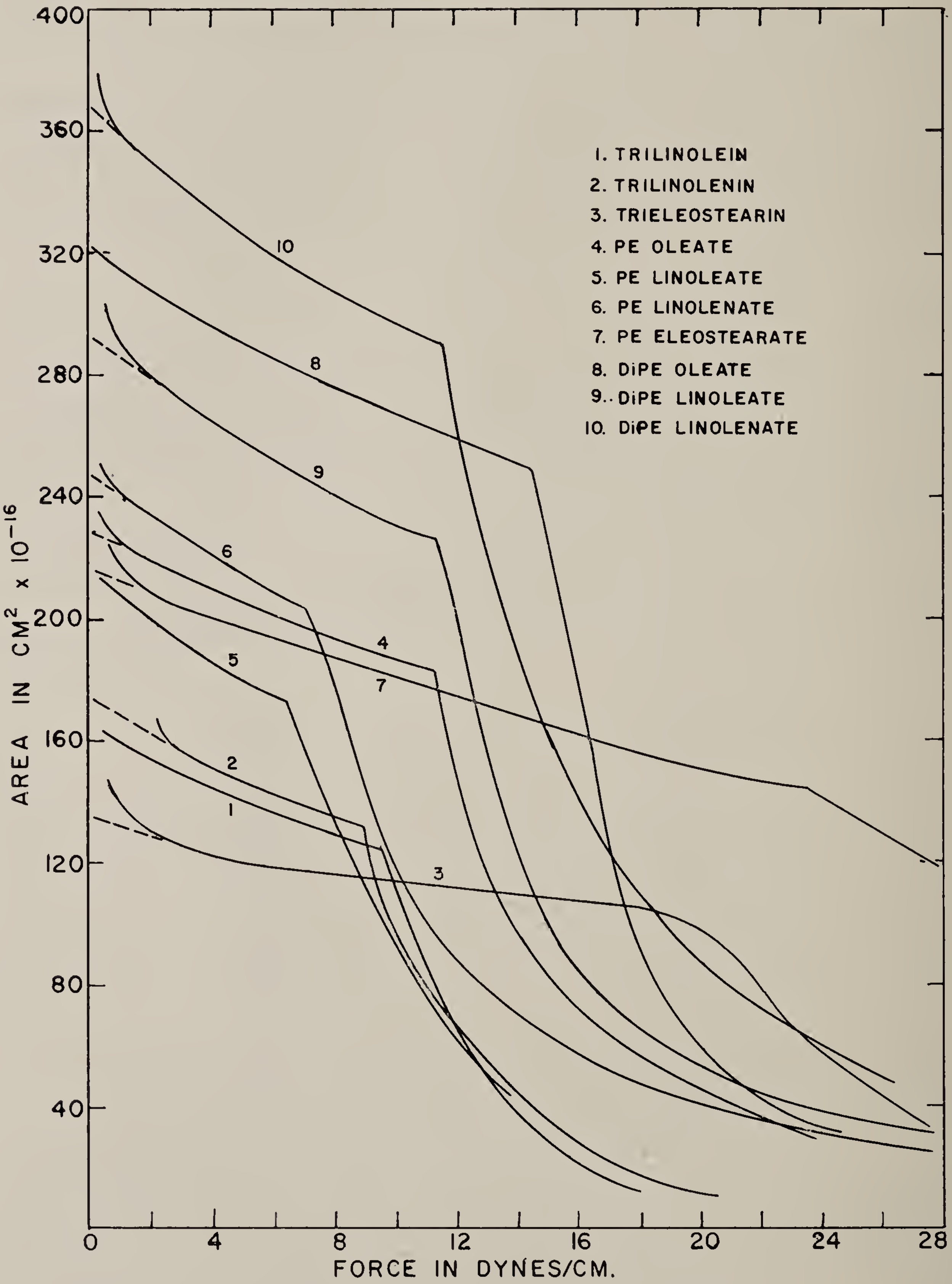

Fig. XII-2. Force-area curves for esters.

and for those which were exposed to air in Fig. XII-3. Those for trilinolein and trilinolenin are quite similar; both exhibit a sharp break at the crumpling point of the films. All the compounds containing oleic, linoleic, and linolenic acids showed relatively sharp breaks.

It is seen that the molecular cross-sectional area for trieleostearin was a little less than for the unconjugated compounds, but that greater force was required to cause crumpling. The curves for all the eleostearic compounds broke less sharply. Since this was true also ol curves of partially oxidized trilinolein and trilinolenin, and since eleostearic compounds are particularly susceptible to oxidation, this lack of sharpness at their crumpling points may be ascribed to an appreciable amount of oxidation that occurred, even during the short time taken in the measurements.

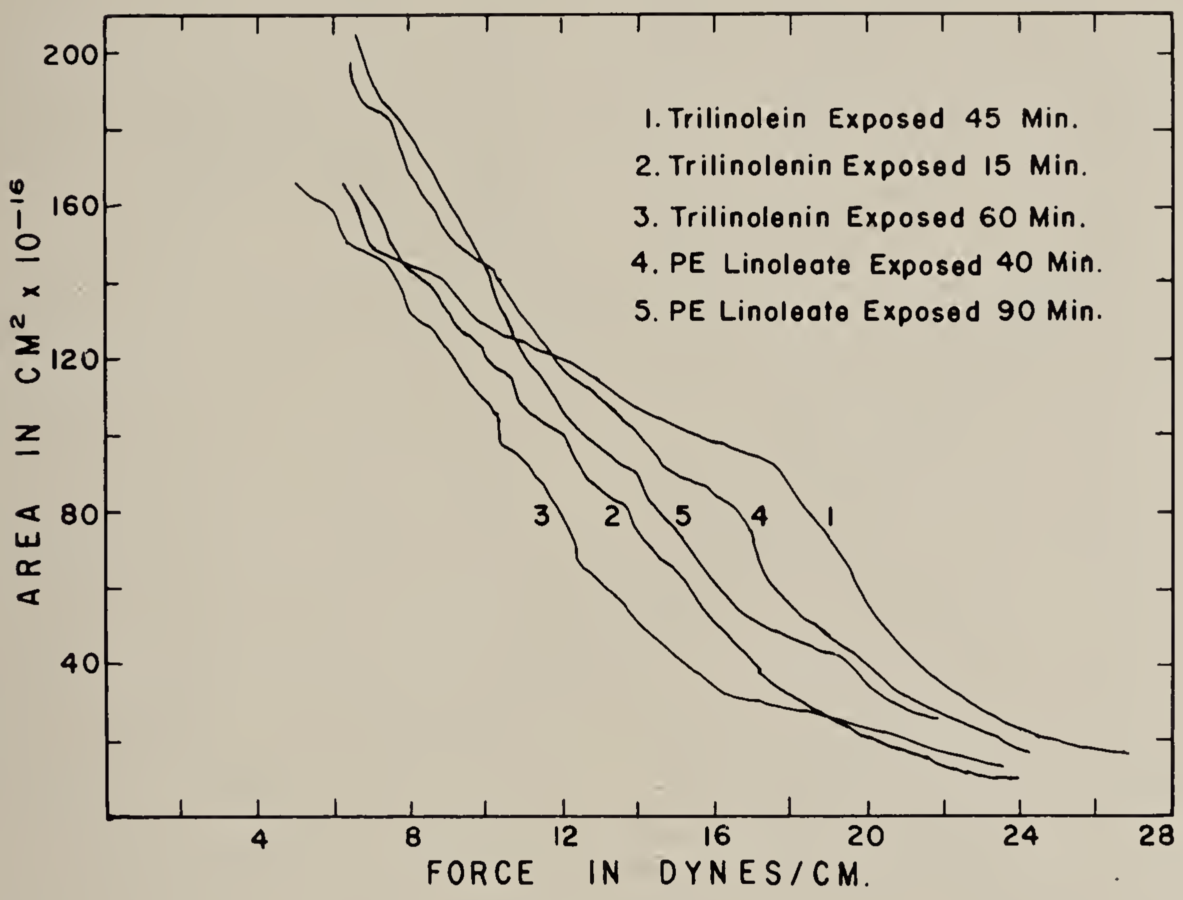

Fig. XII-3. Force-area curves for esters after exposure to air.

Figures XII-4 and XII-5 illustrate typical curves obtained with the alkyds (one illustrative curve of force times area is included). That for SO oleic PE alkyd, which had the highest average molecular weight of any of these resins, broke sharply, even though there must have been a considerable deviation of individual molecular weights from the average. This indicates that the molecules, although of different sizes, were oriented according to some common pattern.

Further evidence of such a common pattern of orientation for all molecules was that the equation of state $F(A - b) = Ktx$ was applicable to the portions of the curves up to the crumpling point almost as well for the alkyds as for the esters.

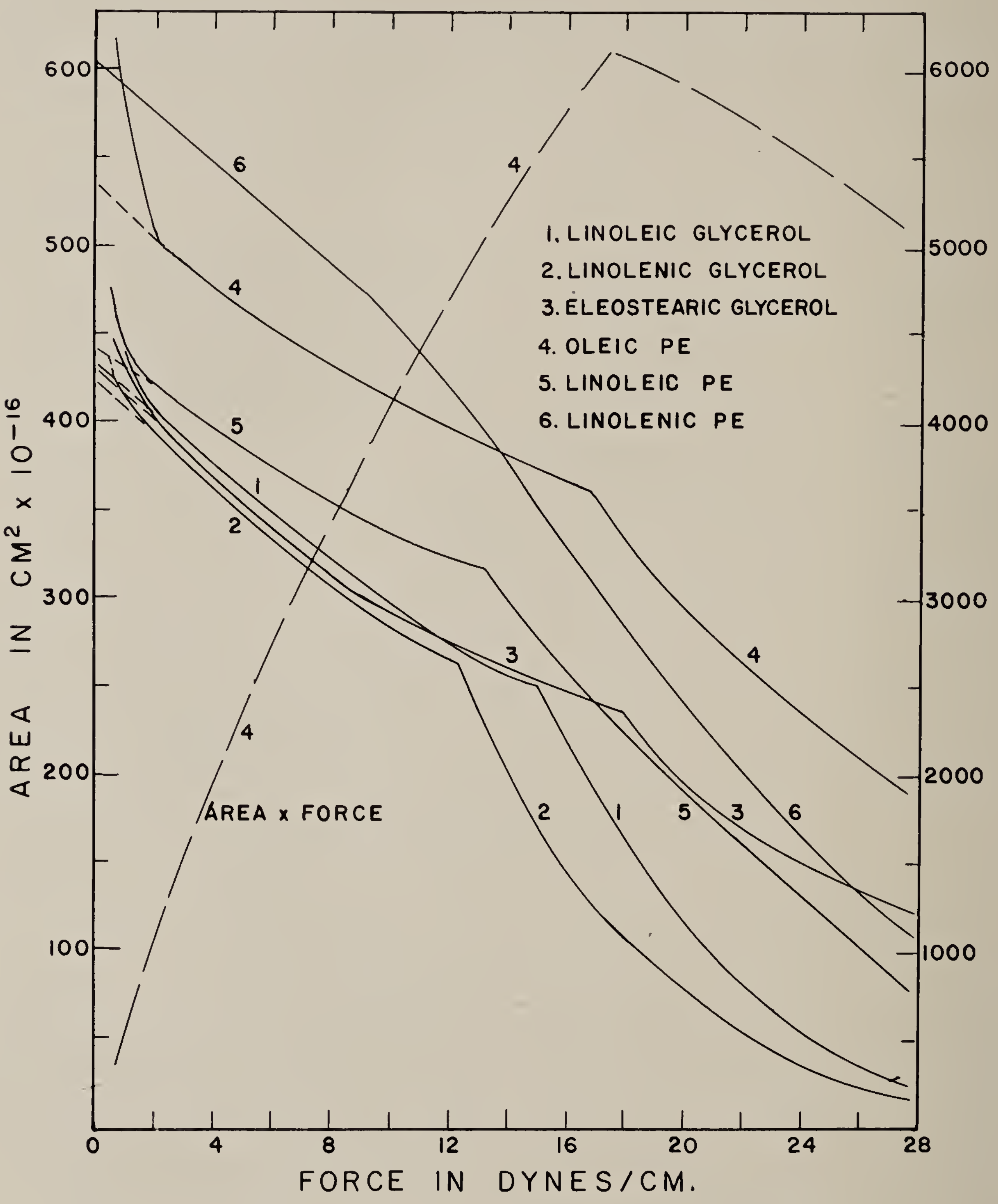

Fig. XII-4. Force-area curves for long-oil alkyds.

TABLE XII-2

Molecular Dimensions of Federation Compounds and of Fatty Acids

Material	A_i (cm.^{2} × 10^{-16})	A_0 (cm.^{2} × 10^{-16})	A_c (cm.^{2} × 10^{-16})	F_c (dynes/ cm.)	H_0 (cm. × 10^{-8})	H_c (cm. × 10^{-8})
Trilinolein	164	179	127	11.3	8.72	12.28
Trilinolenin	164	183	136	8.9	8.45	11.37
Trieleostearin	150	136	102	19.6	11.22	14.97
PE oleate	240	228	185	11.1	9.30	11.46
PE linoleate	205	213	174	10.2	9.84	12.07
PE linolenate	250	249	199	11.2	8.39	10.51
PE eleostearate	202	200	121	18.4	10.45	17.28
DiPE oleate	300	326	251	14.5	10.04	13.03
DiPE linoleate	288	293	227	11.4	11.09	14.32
DiPE linolenate	401	377	299	11.1	8.54	10.78
Oleic acid		66	31.5	27.6	8.27	17.32
Linoleic acid		62	23	25.9	8.25	22.25
Linolenic acid		66.5	20	20.1	7.55	25.10
LO linoleic glycerol alkyd	433	426	251	14.8	9.29	15.78
LO linolenic glycerol alkyd	416	443	263	12.1	9.56	16.10
LO eleostearic glycerol alkyd	431	425	234	17.9	11.53	20.95
SO linoleic glycerol alkyd	908	849	388	18.6	8.23	18.00
SO linolenic glycerol alkyd	821	801	392	16.8	9.32	19.04
SO eleostearic glycerol alkyd	818	811	373	26.0	9.21	20.00
LO oleic PE alkyd	621	537	357	16.8	9.98	15.02
LO linoleic PE alkyd	478	438	318	14.3	12.88	17.74
LO linolenic PE alkyd	596	610	475	9.2	9.59	12.32
SO oleic PE alkyd	1797	1845	1090	20.2	8.28	14.01

Key: A_i, area per molecule at initial reading; A_0, area per molecule at 0 film pressure; A_c, area per molecule at crumpling point; F_c, force at crumpling point; H_0, height of molecule at 0 film pressure; H_c, height of molecule at crumpling point.

Tables XII-2 and XII-3 contain a summary of the data from the force-area measurements. Molecular cross-sectional areas at three pressures (initial; extrapolated to zero pressure; and at the crumpling point) were calculated from the formula

$$\text{Molecular area} = \frac{14\ (\text{distance})\ (\text{drops per ml.})\ (250)\ (\text{mol. wt.})}{(\text{drops})\ (\text{grams sample in 250 ml.})\ (6.06 \times 10^{23})}$$

Figures in the other columns of Table XII-2 were obtained by use of the following relations:

$$\text{Molecular volume} = \frac{\text{mol. wt.}}{(\text{specific gravity})\ (6.06 \times 10^{23})}$$

$$\text{Height of molecule } (H) = \frac{\text{molecular volume}}{\text{molecular area}}$$

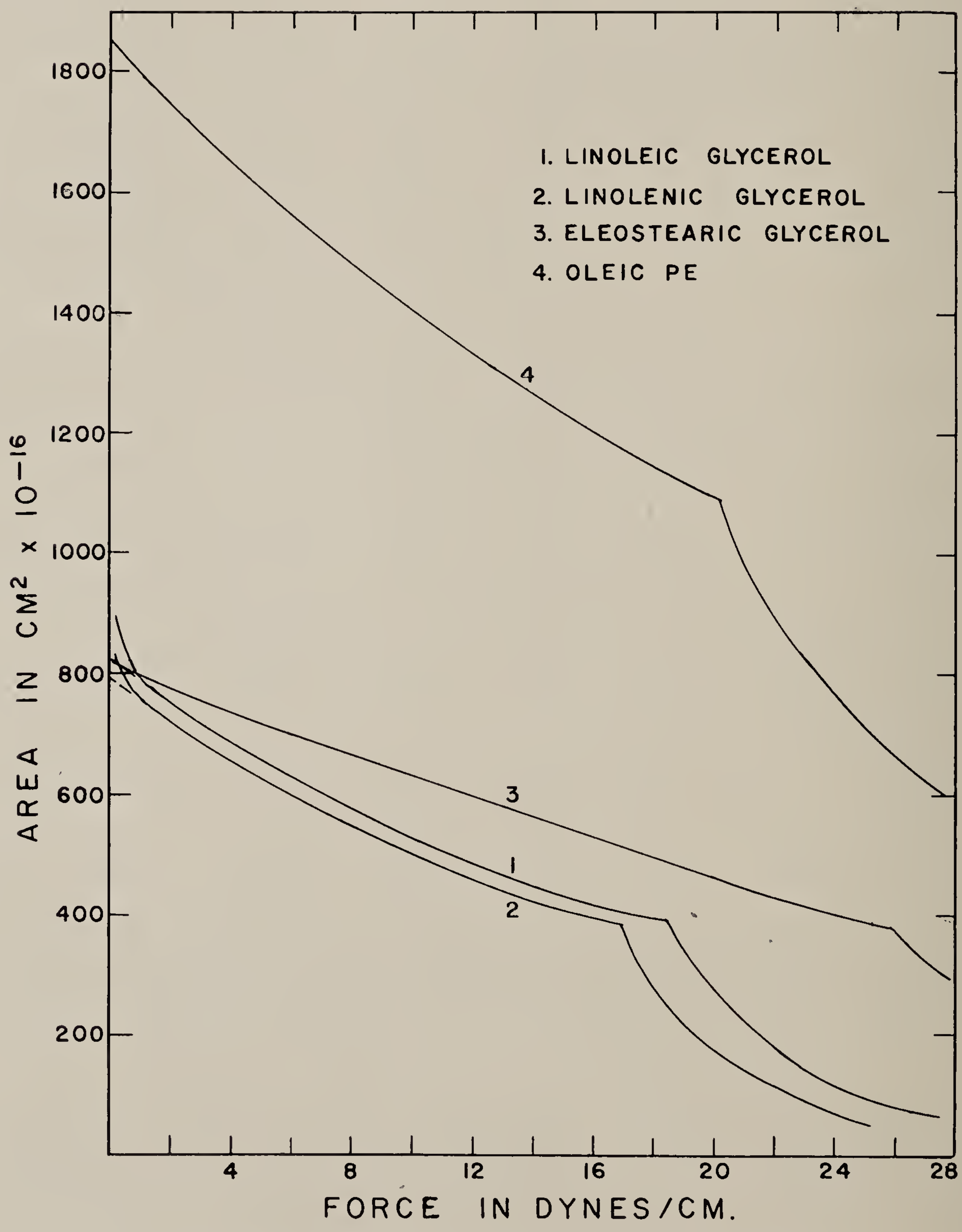

Fig. XII-5. Force-area curves for short-oil alkyds.

In Table XII-3 the constants x and b were calculated from the equation $FA = KTx + Fb$, where $K =$ Boltzmann's constant, 1.38×10^{-16}.

As expected, the areas and the film densities for the esters in Table XII-2, either at zero pressure or at the crumpling point, increase with the number of fatty acid radicals per molecule, but

TABLE XII-3

Constants for Equation of State $FA = KTx - Fb$

Compound	A_c (cm.$^2 \times 10^{-16}$)	b (cm.$^2 \times 10^{-16}$)	x
Trilinolein	127	117	0.345
Trilinolenin	136	121	0.301
Trieleostearin	102	103	0.210
PE oleate	185	181	0.393
PE linoleate	174	166	0.170
PE linolenate	199	191	0.346
PE eleostearate	121	132	0.423
DiPE oleate	251	248	0.45
DiPE linoleate	227	215	0.388
DiPE linolenate	299	307	0.270
Oleic acid	31.5	27.6	0.337
Linoleic acid	23	25.9	0.262
LO linoleic glycerol alkyd	251	284	0.597
LO linolenic glycerol alkyd	263	295	0.575
LO eleostearic glycerol alkyd	234	267	0.691
SO linoleic glycerol alkyd	388	468	1.45
SO linolenic glycerol alkyd	392	452	1.94
SO eleostearic glycerol alkyd	372	571	1.19
LO oleic PE alkyd	357	371	1.02
LO linoleic PE alkyd	318	332	0.539
LO linolenic PE alkyd	475	470	0.513
SO oleic PE alkyd	1090	1135	3.02

not in direct proportion. The only exception is shown by the free acids at the crumpling point; it would be expected that these acids could pack more closely than the esters before rupture of the film structure occurred.

Short-oil alkyds are seen to be generally larger in area than those long in oil, as would be expected from the ratio of their structural units. Noticeable also is the wider difference for the alkyds between areas at zero pressure and at the crumpling point; in other words, the alkyds spread more readily on water than do the oils.

Discussion

The data of this study led the authors to these conclusions.

1. The spreading effect of various compounds, as related to acid component, is least for those containing eleostearic acid and increases in the order linoleic and oleic to linolenic.

2. If the relative heights of the ester molecules indicate less rigidity in structure, the eleostearic chain is most flexible, the linolenic least so.

3. The force at crumpling point is greatest for eleostearic compounds, least for linolenic; as to the alcohol component, it is greatest for diPE, least for glycerol esters. The area also is greatest for diPE, least for glycerol esters.

4. All the compounds exhibit vapor- and liquid-expanded phases, but there is some evidence of intermediate and liquid-condensed phases in the curves of some of the alkyds.

5. The constant b in the equation of state is almost identical with the area at the crumpling point; it appears to be the limiting area factor in the crumpling of the film.

6. The constants x for the esters agreed with one another rather well.

7. The constants x for those alkyds containing mineral spirits showed good agreement. Diisobutyl ketone used as reducer in the others formed a monolayer along with that of the alkyd, causing variations in both constants x and b.

8. Force-area measurements not only suggest differences in the wetting properties of various products on hydrophilic surfaces; they can also provide data of a very fundamental nature for routine control purposes, to show differences from batch to batch, and to suggest to a formulator reasons why one batch or one vehicle behaves differently from another.

Evaluation

In evaluating the force-area measurements, Dr. I. M. Bernstein preferred to take the actual initial area reading A_i in each case, rather than the A_0 figure (extrapolated to zero compression) which was used by Long and Lawton.

Trilinolein and Trilinolenin

The fact that trilinolenin has approximately the same initial area (about 164) as trilinolein but a greater area at crumpling (136 vs. 127) may be due to a difference in geometric isomerism (arising from the possible presence of more *trans* double bonds in the linolenic acid prepared by debromination) or to a more hydrophilic character of the more unsaturated compound. The lower force F_c at film crumpling, 8.9 for trilinolenin compared with 11.3 for trilinolein, indicates perhaps that the three double bonds impart greater rigidity, requiring less force to move the molecule to the final film crumpling position and none to overcome flexibility in the molecule itself—a view contrary to that of Long and Lawton.

Effect of air exposure. The initial areas of these films after exposure were approximately the same as for unoxidized films, but those at crumpling pressures were lower. The transformation from nonconjugation to conjugation, concurrent with oxidation, may explain this; unoxidized conjugated oils showed consistently a lower A_c than the unoxidized nonconjugated. However, an inconsistency is noted in that, for trilinolenin, the A_c value after decreasing from 134 to 116 after 15 minutes exposure climbed again to 122 after 60 minutes oxidation. Nor does the smaller F_c value, 9.2 after this exposure as compared with 10.8 after 15 minutes, fit in with the assumed oxidation-conjugation relationship, for the crumpling force for conjugated oils is around 20. A longer exposure time than 1 hour might have established a significant trend. Crumpling points for air-exposed films, except for 15-minute trilinolein, could not be obtained directly from the force-area diagrams because the break was indistinct; it was taken as the point at which the curve for area times force, plotted against force, reached a maximum. In most runs, the maximum was quite sharp and it coincided with the crumpling breaks, where these were distinguishable.

Trieleostearin

The area at initial measurement is about 10% less than that for trilinolein and trilinolenin; the difference at the crumpling point is even greater (102 vs. 127 and 136). Different isomeric form, with a smaller or more sharply defined water contact area, may account for the smaller initial area. The much smaller area, and particularly the high force (19.6) at crumpling, may indicate a greater degree of compressibility of the molecule, or greater secondary valence forces to be overcome in this and other conjugated systems, which are distinguished by similar attributes.

PE Esters, before and after Exposure

The PE oleate and linolenate have considerably higher A_i values than the linoleate, all of course higher than corresponding glycerides, but force at crumpling differs very little. Values of A_c vary in the same order.

PE linoleate films exposed for 40 and 90 minutes show, surprisingly, the same A_i value as the unoxidized one; however, the area at crumpling decreased markedly. There was little increase in F_c values, from 9.2 for the unoxidized to 9.5 for the two exposed films; but since these A_c and F_c values were obtained by the indirect method, they may not be too significant. The trend of a decrease in A_c with little change in F_c on oxidation is the same as for trilinolein. Possibly the decrease in A_c may mean that the hydrophilic part of the molecule is geometrically more sharply defined under stress, in contact with water.

PE eleostearate follows the pattern of trieleostearin in exhibiting much lower areas, both initial and at crumpling, than the corresponding oleate and linoleate; surprisingly, however, its A_i value is not much lower than that of PE linoleate. Force at crumpling, as for trieleostearin, is high. Air exposure readings for these eleostearic compounds (unfortunately not made) might have contributed substantially to the total picture.

DiPE Esters

The oleate, linoleate, and linolenate were, as expected, larger in area, both initially and at crumpling, than the corresponding PE compounds. The respective order is the same but the spread between linolenate and oleate is greater in this series.

Bernstein sees in the difference in areas between linolenates and oleates a possibility that the larger number of double bonds in the fatty acid component may impart a stronger hydrophilic character to the molecule. At least at the crumpling point, the oleates would show under compression a greater area of water contact. Langmuir

(16) in 1917 noted similar behavior. The A_c values of 31.5 for oleic, 23 for linoleic, and 20 for linolenic acid corroborate this general point, although the oleate esters come second in A_i and A_c values, whereas theoretically they should come third. Geometric isomerism may come into play as an additional factor. Great difficulties lie in the way of determining experimentally the actual points of a geometrically complex structure which are in contact with the water at the crumpling point or even initially. This information, however, has little bearing on the mechanism by which such films dry, even assuming the presence of an adsorbed water layer on the surface being coated.

Contrary to the expectation that a large force would be needed to crumple a film containing such large molecules, the diPE esters required only an average of 12.3 as against 10.8 for the corresponding PE and 10 for the glyceryl compounds. The highest F_c value, 14.5 for diPE oleate, is still much less than the approximate value of 20 for the conjugated trieleostearin and PE eleostearate.

Alkyds

As expected, molecular cross-sectional areas for both long- and short-oil alkyds are considerably higher than for the corresponding oils. For the long-oil alkyds, where the diluting effect of glyceryl phthalate is less, the pattern of areas and forces resembles that of the oils; the short-oil compounds are less predictable. Thus in contrast to the much lower A_i and A_c values for the conjugated than for the nonconjugated glyceryl oils, those for the corresponding SO eleostearic glycerol alkyd are only slightly lower than those for the nonconjugated SO glycerol alkyds. The SO oleic PE alkyd, on the other hand, shows significantly larger areas. Whereas the F_c values for the nonconjugated short-oil alkyds are higher than those for glyceryl and PE oils (approaching those for conjugated oils), that for the SO eleostearic glycerol alkyd also shows an increase to a new high value of 26; but the increase is not a proportional one, undoubtedly because of the diluting effect of the phthalate on the percentage of conjugation.

As a control instrument the hydrophil balance can provide useful everyday insight into the makeup of coating molecules, supplementing the usual tests for body, color, drying time, flexibility, etc. Its manipulation is easily learned and its cost is moderate.

Long and Lawton suggested additional reading for those interested in the subject. Some selected references are included here.

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CHAPTER XIII

Oxidation Studies

In the course of studies on the projects previously described, it became evident that something more was needed to tie together the data obtained. Not enough fundamental information was being gathered on the chemical changes involved in film formation to explain why the different compounds behaved as they did. The ultraviolet and infrared spectrophotometric studies had confirmed that peroxides were formed at varying rates and to varying extents, and that changes in conjugation took place, but did not sufficiently measure these changes nor relate them with each other to demonstrate how they affected the properties of films.

Project 24 was undertaken in the attempt to wring from the small quantities of compounds still available as much of this fundamental information as possible, and to relate the amounts and rates of oxygen absorption with those of peroxide formation and the shifting of double bonds. Films of some of the vehicles, starting with no conjugation, produced small amounts of compounds containing as many as four sets of double bonds on adjoining pairs of carbon atoms; others lost conjugation from the moment of exposure to air.

In a second phase of this project, more comprehensive studies were made of trilinolein and trilinolenin, of which larger lots had been prepared. Some of the spectrophotometric data obtained in this part of the work have already been presented in Chapter V, but the remainder of the project is recounted here.

Oxygen Absorption, Peroxide Accumulation, Spectral Changes, Project 24—The Hormel Institute

First Phase: General Studies of All Compounds

Dr. Lundberg was in direct charge of this study and was assisted by Drs. J. R. Chipault, E. C. Nickell, and Evelyn McMeans. Reports appeared in the *Official Digest,* No. 322, 740 (November, 1951); No. 328, 319 (May, 1952); and Vol. 26, 548 (July, 1954).

Procedures; Equipment

Oxygen absorption measurements were made in a modified Warburg apparatus. The bath was a stainless steel tank 12 × 24 × 10 inches deep, with a frosted glass bottom. It had an efficient stirrer, and the temperature was maintained at 25° C. by means of a heating element with mercury thermoregulator, and a cooling coil for use in warm weather. A daylight fluorescent lamp placed directly under the bath, and masked where necessary, provided uniform illumination of 25 foot-candles at the level of the films.

The Warburg manometers were mounted on adjustable supports and placed in the bath. The supports were manipulated individually until the bottom of each flask was perfectly level and then locked in place. Thereafter the position of the manometers was not changed, and each flask was always placed in the same position on its own manometer. The flasks were flushed with air which had been brought to 50% relative humidity by passing through a saturated solution of calcium nitrate at 25° C.

The reaction vessels were cylindrical flasks from which the original slightly concave bottoms had been removed; pieces of flat pyrex glass sealed on to replace them insured a flat lower surface on which films of uniform thickness could be spread. The internal diameter of the bottoms was 54 mm; the total volume of the flasks varied from 47 to 65 ml. Nitrogen, purified over hot copper gauze, was available for all manipulations that required protection of the materials from air.

Spectral measurements were obtained with a model DU Beckman spectrophotometer.

Preparation of Ester Samples

By means of a 2-ml. hypodermic syringe well flushed with nitrogen, about 1 gram of compound was transferred from its freshly opened ampule to a nitrogen-filled tared test tube drawn to a constricted opening, and quickly weighed. Another syringe introduced 0.1 ml. of standard drier solution for each gram of sample; the tube was evacuated, flushed repeatedly with nitrogen, and sealed under vacuum. Contents of the tube were well mixed, and allowed to stand in the dark at about 25° C. for 48 hours.

At the end of this aging period, the sample was transferred to a volumetric flask and dissolved in cold air-free isopentane. An aliquot of the solution containing enough material to lay a 1.25-mil film was placed in a tared Warburg flask which had been flushed with nitrogen, and spread uniformly on the level bottom of the flask. The solvent was evaporated in a stream of nitrogen. A quick weighing gave the exact amount of sample used. Four to six samples were measured rapidly into flasks in this way and kept under nitrogen until all samples had been weighed. The flasks were then fastened to their respective manometers and immersed in the bath. A slow current of air at 25° C. and at 50% R.H. was passed over the samples for 1 minute. Air flow was then stopped, and, after a 1-minute equilibration period, manometers were closed and oxygen absorption measurements begun. At this time, one of the samples was removed and used to determine the initial peroxide value (P.V.) and spectral characteristics.

Lest a low oxygen supply become a limiting factor in the oxidation, the manometers were reset and the flasks reflushed and re-equilibrated at intervals. Corrections were made for the amount of oxygen absorbed during this operation.

Examination of Film and Determination of Peroxide Values

After a selected degree of oxidation had been reached, a flask was removed from the bath and immediately flushed with nitrogen. Both openings were covered with a piece of dental rubber dam. A thin nitrogen inlet tube was introduced through a pinhole in the dam covering the main opening; a pinhole in the dam over the other opening served as a gas outlet. At this point the physical condition of the film was determined by gentle probing with the small inlet tube. If it was easily scratched but not tacky and no material stuck to the tube, it was considered "set." If it was scratched with difficulty and chipped under forced probing, it was described as "hard."

The peroxide values were then determined iodimetrically, directly in the Warburg flask in the absence of air (5). The chloroform–acetic acid solvent (3:2), prior to use, was kept in a small beaker covered with a rubber dam and freed of oxygen by flushing with a stream of nitrogen. A freshly made saturated solution of potassium iodide in aldehyde-free methanol was similarly freed and protected from air. The reagents were taken from their containers and introduced into the Warburg flasks by means of hypodermic syringes. Five milliliters of solvent, followed by 2 ml. of iodide solution, were added to the sample and the flask was placed in a bath at 35° C. under nitrogen. When the films were soluble in the solvent, a 15-minute reaction time was sufficient, but where insoluble films had formed, 2.5 hours were allowed for completion of the reaction. Auxiliary experiments proved that no oxidation of iodide by the insoluble films took place after a 2-hour reaction period. After addition of 10 ml. of air-free water, the liberated iodine was titrated with 0.01 *N* sodium thiosulfate. Peroxide value and oxygen absorption were calculated as moles of O_2 per mole of fatty acid.

Measurement of Spectral Absorption

Previous studies (6) showed that the ultraviolet spectral absorption of the products of reduction of linoleate peroxides in bulk with KI was virtually the same as the spectral absorption of the peroxides. However, auxiliary experiments on linseed oil films under the conditions of this study revealed that the reduction of such films, oxidized to various oxygen absorption levels up to 5170 meq. per kilogram, caused decreases of 10 to 20% in the ultraviolet absorption in the conjugated diene region. Table XIII-1 summarizes the results.

TABLE XIII-1
Effect of Reduction by Iodide on the Spectral Characteristics of Oxidized Linseed Oil Films

		α at 2320–30 A		α at 2690 A	
O_2 absorption (meq./kilo)	P.V. (meq./kilo)	Before reduction	After reduction	Before reduction	After reduction
1015	810	7.10	6.45	1.20	1.43
2010	945	8.73	6.94	1.37	1.89
2555	1250	7.75	6.80	1.33	1.81
4030	1930	7.30	7.61	1.36	2.37
5170	1740	8.98	7.70	1.37	2.82

Because of the limited amount of sample, all measurements of ultraviolet spectral absorption in this study were made on the residues from the peroxide value determinations. Therefore the values presented must be regarded as minimum values; deductions made from the data must be interpreted accordingly.

The reduction products from the peroxide determination were recovered by extraction with peroxide-free ethyl ether. After being washed with air-free water until neutral and dried over sodium sulfate, the solution was transferred to a tared volumetric flask and the spectral measurements were made.

In the advanced stages of oxidation where insoluble films were formed, the recovered reduced material was saponified and the spectral absorption of the liberated fatty acids was measured. Auxiliary experiments on oxidized samples of linseed oil showed that saponification of the reduced material caused only about a 5% increase in the conjugated diene absorption and about a 25% increase in that for conjugated trienes.

In the accompanying graphs the vertical line through some of the points indicates that these points represent values for the fatty acids recovered in this manner. The time taken by each compound to attain the highest oxygen absorption level studied is noted to the right of the figures slightly below the abscissa scale.

Preparation of Alkyd Samples

Since the alkyds all contained 50% by weight of either mineral spirits or diisobutyl ketone, some modification of techniques was necessary in preparing samples and also in measuring oxygen absorption. Further, phthalic acid's high nonselective absorption of light in the ultraviolet wavelength regions associated with conjugated dienes and trienes necessitated its removal before spectral changes in the fatty acids could be read.

The procedure for mixing and aging the sample and drier was altered by immersing the lower part of the test tube in a dry ice–acetone bath (to minimize the evaporation of solvent) before evacuating the sample prior to flushing with nitrogen and sealing. At the end of the aging period the sample was transferred to a volumetric flask and dissolved in peroxide-free ethyl ether. Aliquots of the solution sufficient to lay a film of solvent-free alkyd 1.25 mils thick were transferred to the special Warburg flasks; these were immediately mounted on their manometers and oxidation was started.

The exact quantities of alkyd used were determined by measuring another aliquot of the ether solution into a tared suction flask, completely evaporating the solvent under vacuum on a warm water bath, and taking the gain in weight.

Measurement of Oxygen Absorption

The presence of thinners in the alkyds, as well as the solvent introduced with the drier and the ether used to facilitate even distribution of films in a uniform layer, interfered with use of a closed system for oxygen absorption measurements. Oxidation was therefore allowed to proceed with the stopcocks of the Warburg flasks and manometers open and with a slow stream of conditioned air passing over the films. At $^1/_2$-hour intervals the stopcocks were closed and the rates of oxygen absorption were determined over 5-minute periods, after which the stopcocks were again opened.

In an auxiliary experiment the oxygen absorption of the film of a linseed oil solution containing 50% by weight of mineral spirits plus the standard quantity of drier and a little ether was measured in the same manner. At the same time, the oxygen absorption of an undiluted sample of the same linseed oil was measured by the technique employed with the simple esters. In both cases periodic measurements of peroxide values were also made. When these values were plotted against oxygen absorption the curves were found identical. This signified that the more volatile solvents evaporated quickly at the start of each experiment and that errors in oxygen absorption readings due to evaporation of solvent were negligibly small except at the very beginning. In a few cases, the solvent interfered somewhat in the first one or two measurements, and in these the measured rate values were discarded and corrected rate values were obtained by extrapolating subsequent measurements to zero time.

For each sample the observed (or corrected) rates were plotted against time and the area under each curve was taken as a measure of total oxygen absorbed up to the moment of removal from the bath.

The films were probed, and peroxide values determined, in the manner described. Fatty acid content, to which peroxide values were related, was calculated from Wijs iodine values, except for LO eleostearic glycerol alkyd, where the Woburn iodine value method was employed.

Measurement of Spectral Absorption

Phthalic acid in ethyl ether has a specific absorption coefficient of 67 at 2320 Å and 10 at 2680 Å. These high values made it impossible to measure spectral changes in the wavelength regions where conjugated dienes and trienes absorb without first freeing the fatty acids from all traces of phthalic acid. Auxiliary experiments with mixtures of phthalic acid and fatty acids and with the commercial alkyd proved that this could be done, after saponification, by extraction from acid solution with chloroform, in which phthalic acid is insoluble.

As in the case of the esters, the reduced material from peroxide determinations was used for spectral measurements. The reduced compounds were saponified and acidified in the usual manner and the acids extracted with chloroform. After removal of the aqueous layer and precipitated phthalic acid, the chloroform solution was washed several times with water and dried over sodium sulfate. It was then transferred to a tared volumetric flask and the chloroform was evaporated under vacuum. The residue was weighed and dissolved in peroxide-free ether for the spectral measurements.

Results

Absorption of oxygen in relation to time. The data for all compounds are plotted in Figs. XIII-1 to XIII-4. For the simple esters, the approximate relative rates of oxygen absorption were: linolenates, 330; linoleates, 120; eleostearates, 110; oleate, 1. In early stages, trieleostearin absorbed oxygen slightly faster than trilinolein, but after 1 mole had been taken up per mole of fatty acid, its rate decreased more rapidly than that of trilinolein. The rate of PE eleostearate was smaller originally than that of PE linoleate; it also decreased faster in later periods. The LO eleostearic glycerol alkyd absorbed even more slowly. Aside from the eleostearates, alcohol constituents of the molecules influenced the absorption rate only slightly up to a level of 1 mole of fatty acid; beyond this level, the rate for the dipentaerythrityl esters fell off much faster than that of the others, probably because of setting of the film which hindered diffusion.

Among the alkyds, the linoleic compounds oxidized at the same initial rate as the corresponding linolenic materials, and this high

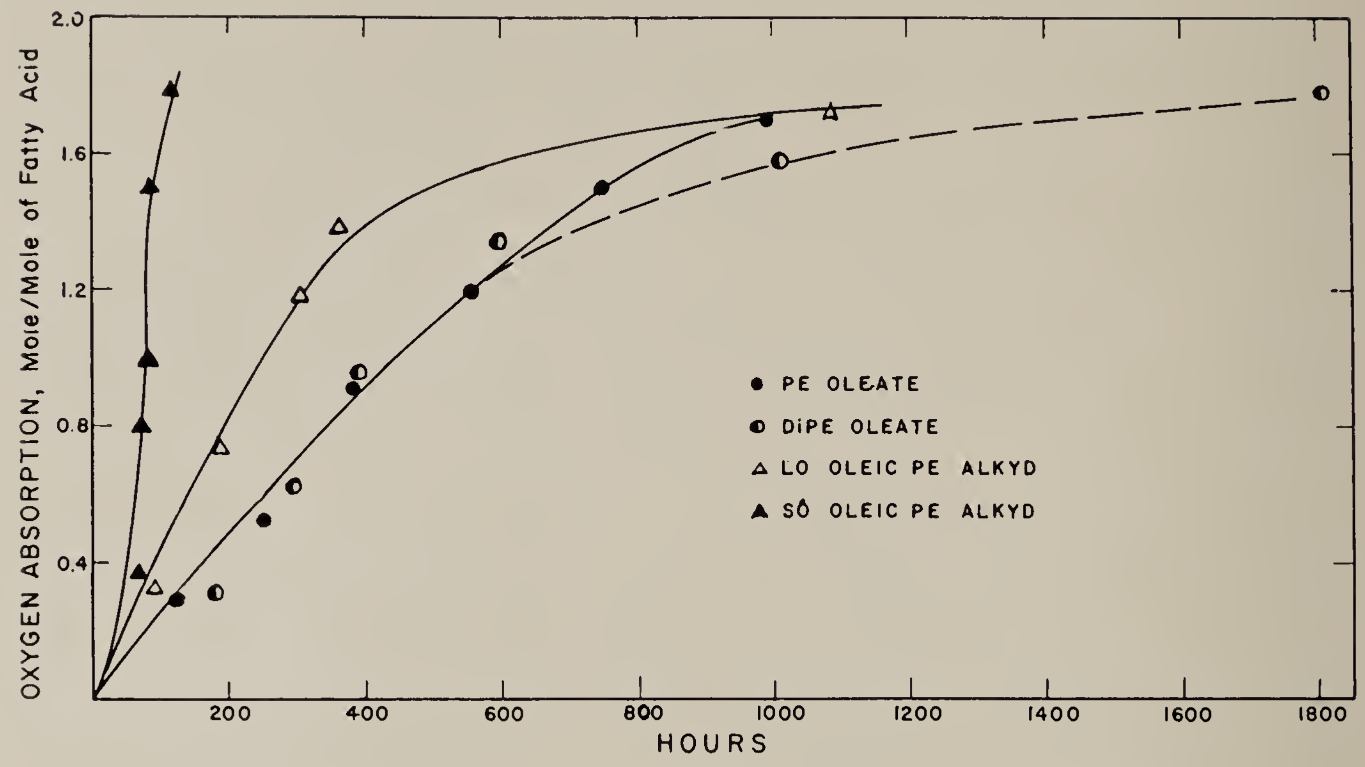

Fig. XIII-1. Rates of oxygen uptake of oleic compounds.

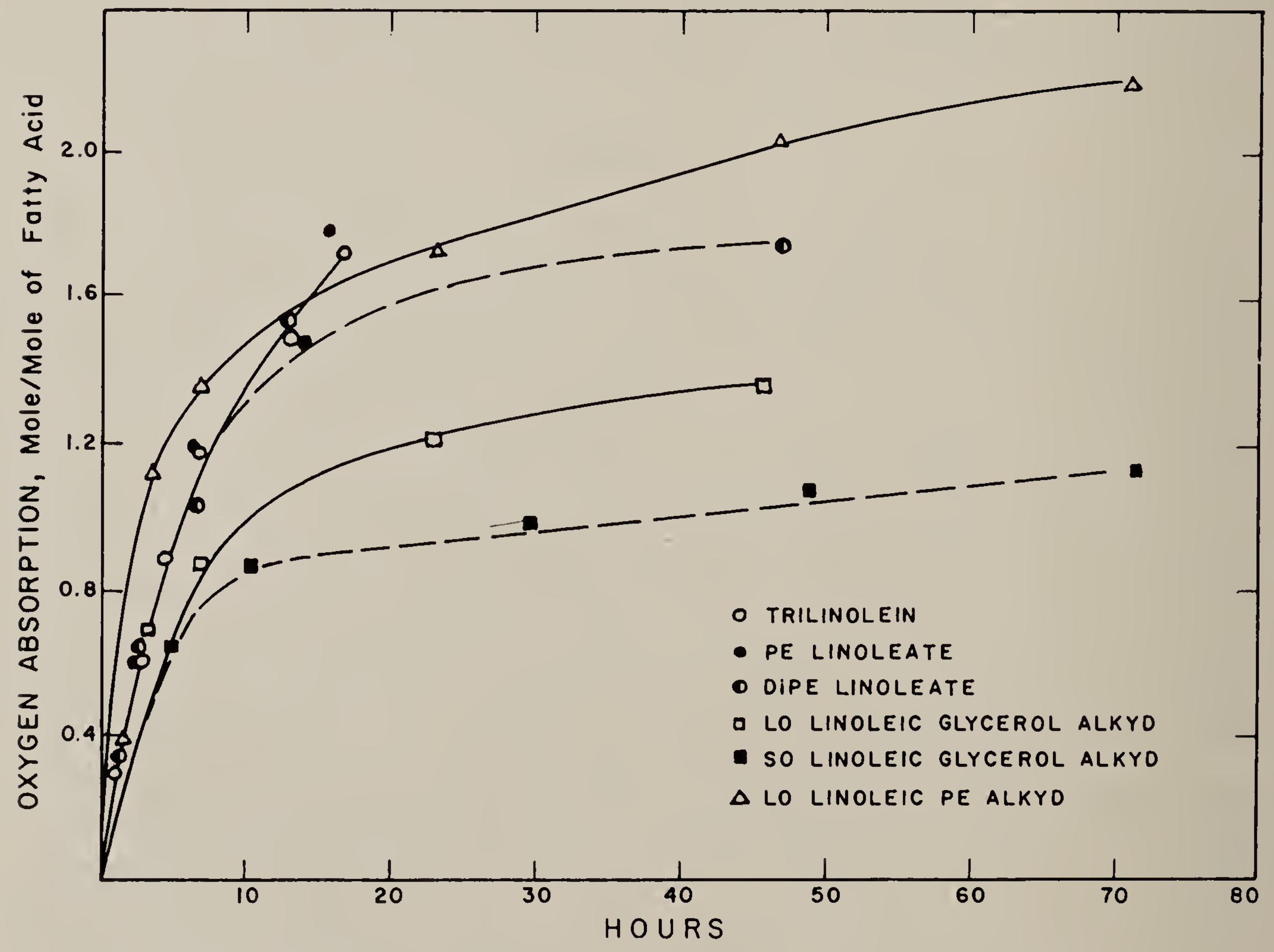

Fig. XIII-2. Rates of oxygen uptake of linoleic compounds.

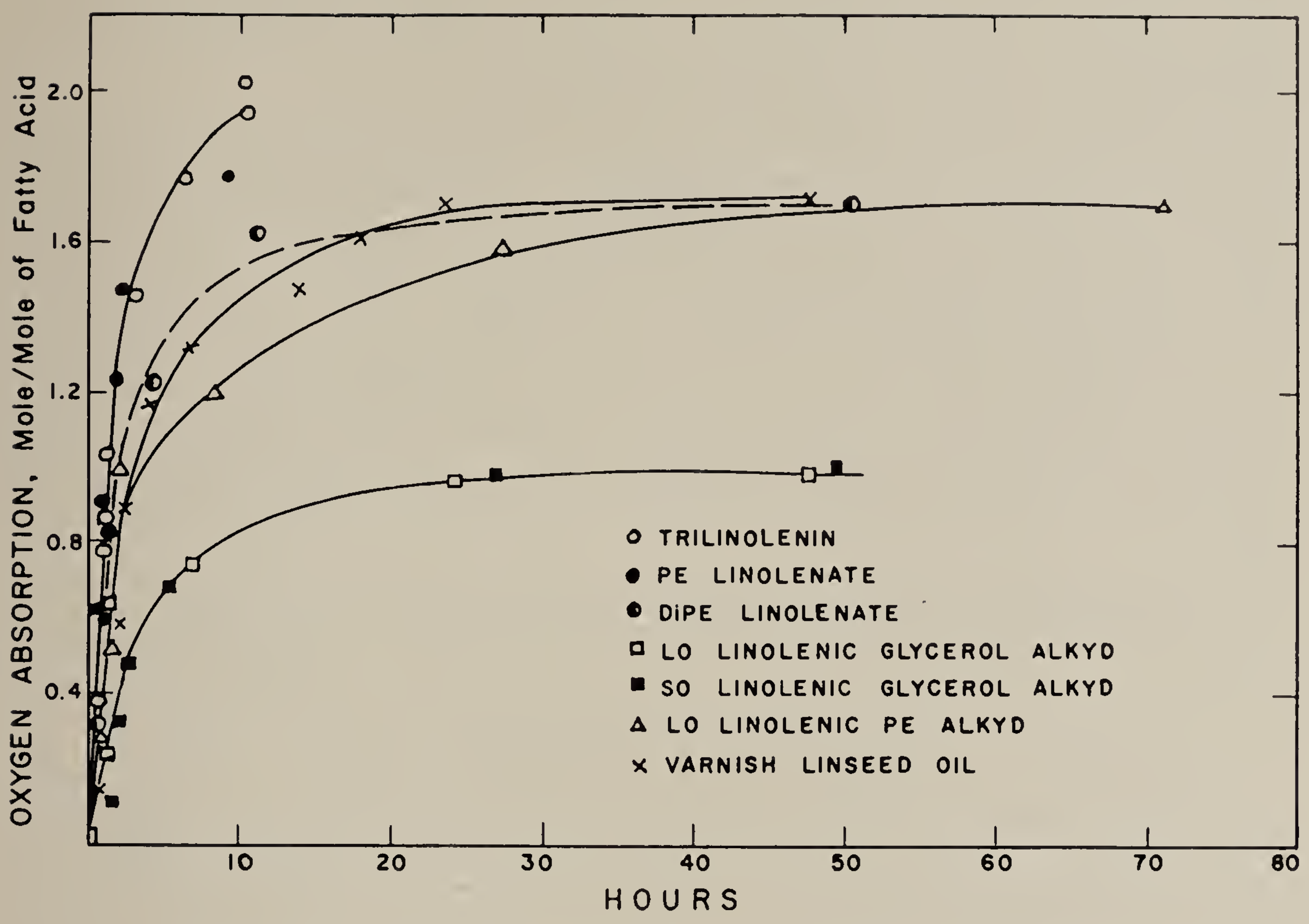

Fig. XIII-3. Rates of oxygen uptake of linolenic compounds.

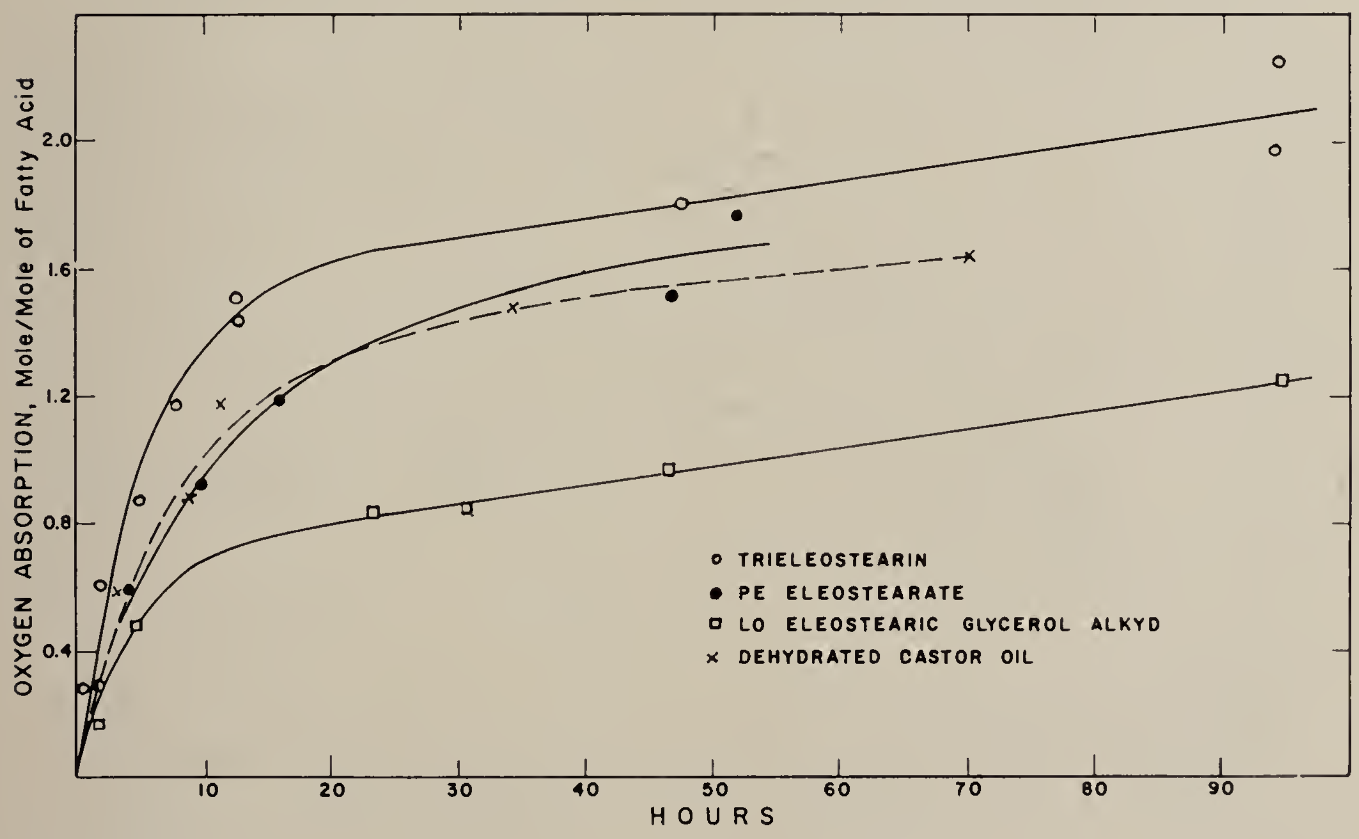

Fig. XIII-4. Rates of oxygen uptake of eleostearic compounds.

initial rate persisted longer with the LO linoleic glycerol and PE alkyds than with the linolenic ones. The rate for PE alkyds was faster than for those containing glycerol.

Oleate compounds absorbed oxygen very slowly but the SO PE alkyd was fastest of the group. The LO PE alkyd was intermediate between the short-oil alkyd and the PE and diPE esters; curves of these two were nearly the same.

The glycerol alkyds of linoleic and linolenic acids, both long- and short-oil, absorbed much more slowly beyond the level of 0.6 to 0.8 mole of oxygen per mole of fatty acid; however, the long-oil PE alkyds of these acids had a rate nearly as high as the corresponding esters.

Varnish linseed oil absorbed at approximately the same rate as diPE linolenate, and dehydrated castor oil at that of PE eleostearate.

General Observations

The results of peroxide and UV spectral measurements appear in Figs. XIII-5 to XIII-24. The data are plotted against "moles of oxygen absorbed per mole of fatty acid," and in the discussion that

Text continues on page 334

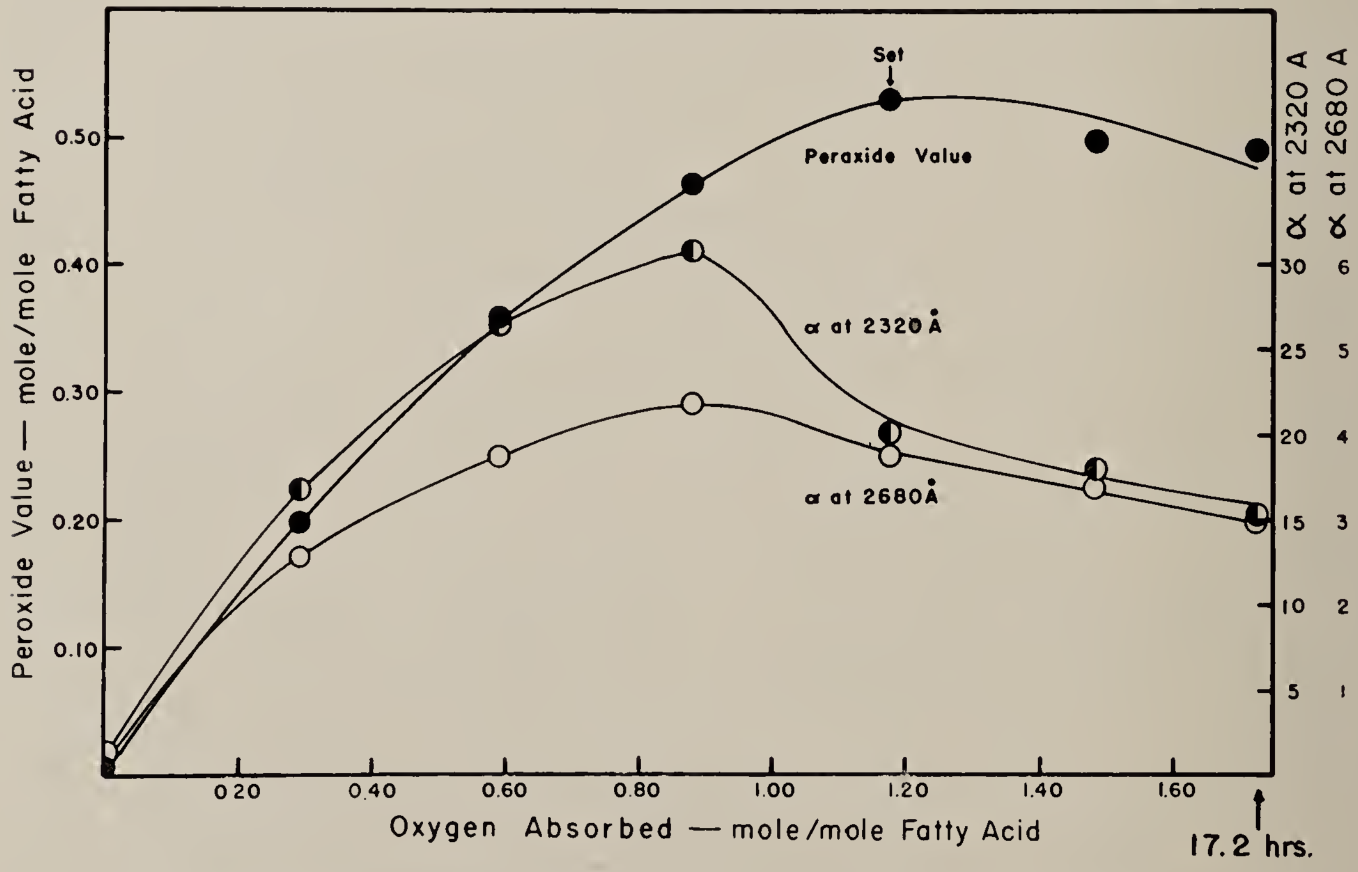

Fig. XIII-5. Changes in peroxide value and UV spectra of oxidizing trilinolein films.

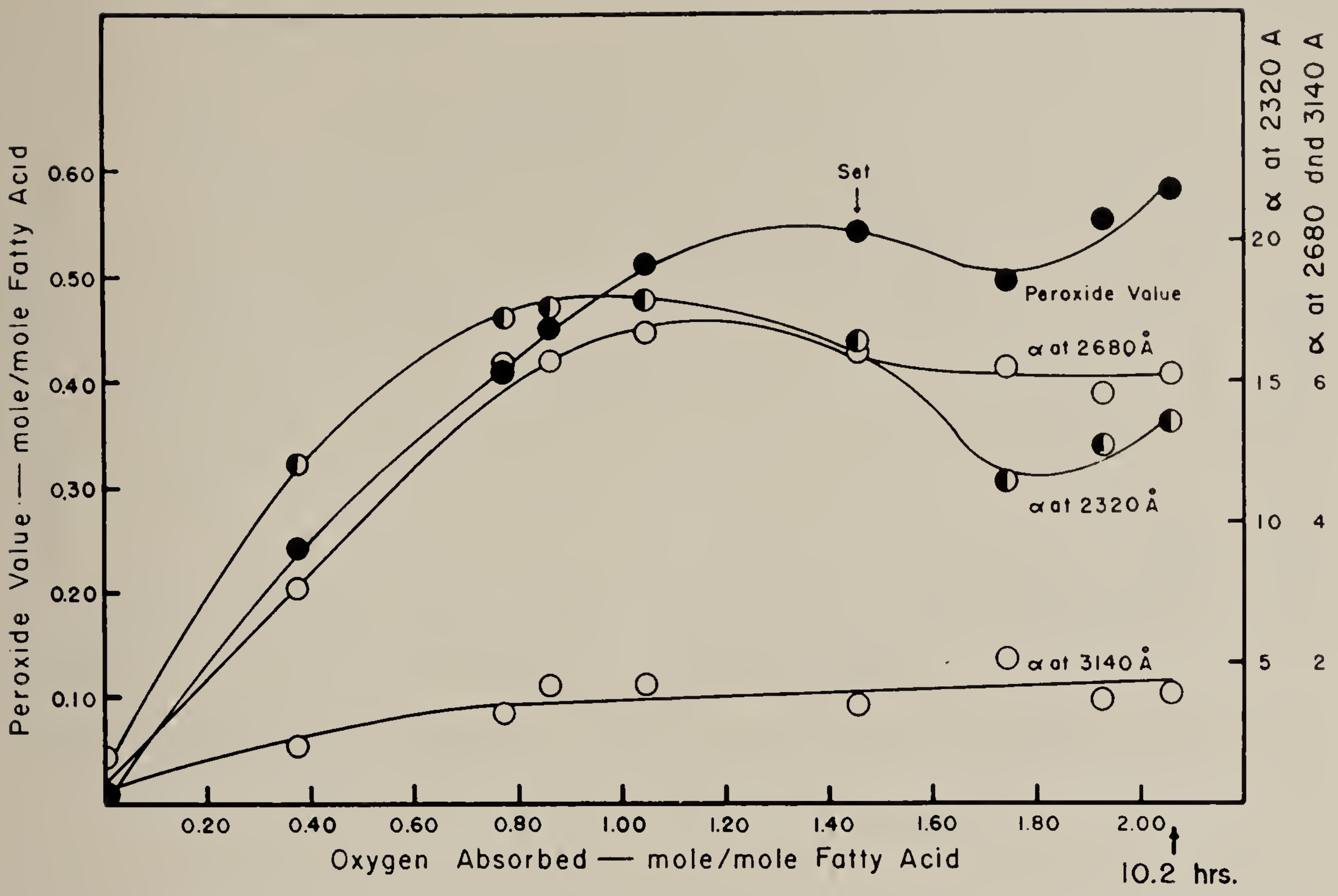

Fig. XIII-6. Changes in peroxide value and UV spectra of oxidizing trilinolenin films.

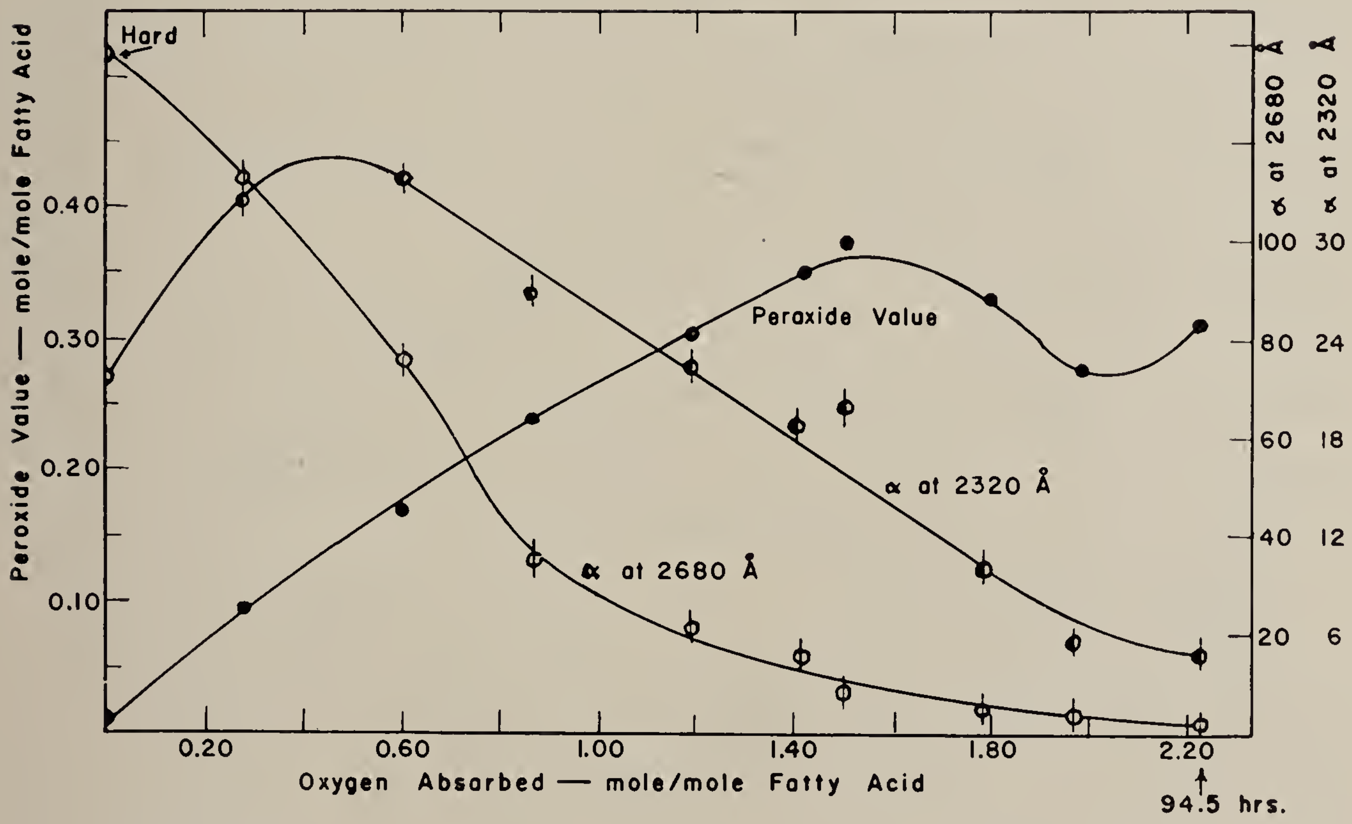

Fig. XIII-7. Changes in peroxide value and UV spectra of oxidizing trieleostearin films.

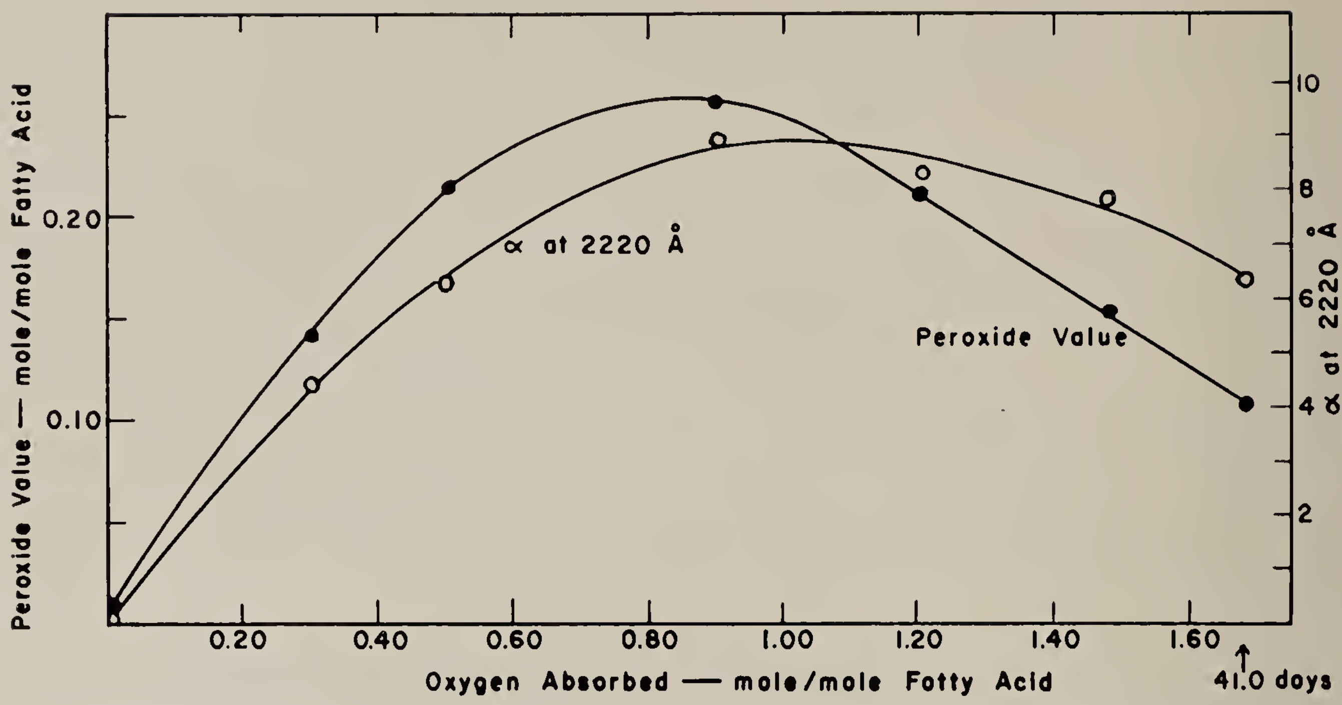

Fig. XIII-8. Changes in peroxide value and UV spectra of oxidizing PE oleate films.

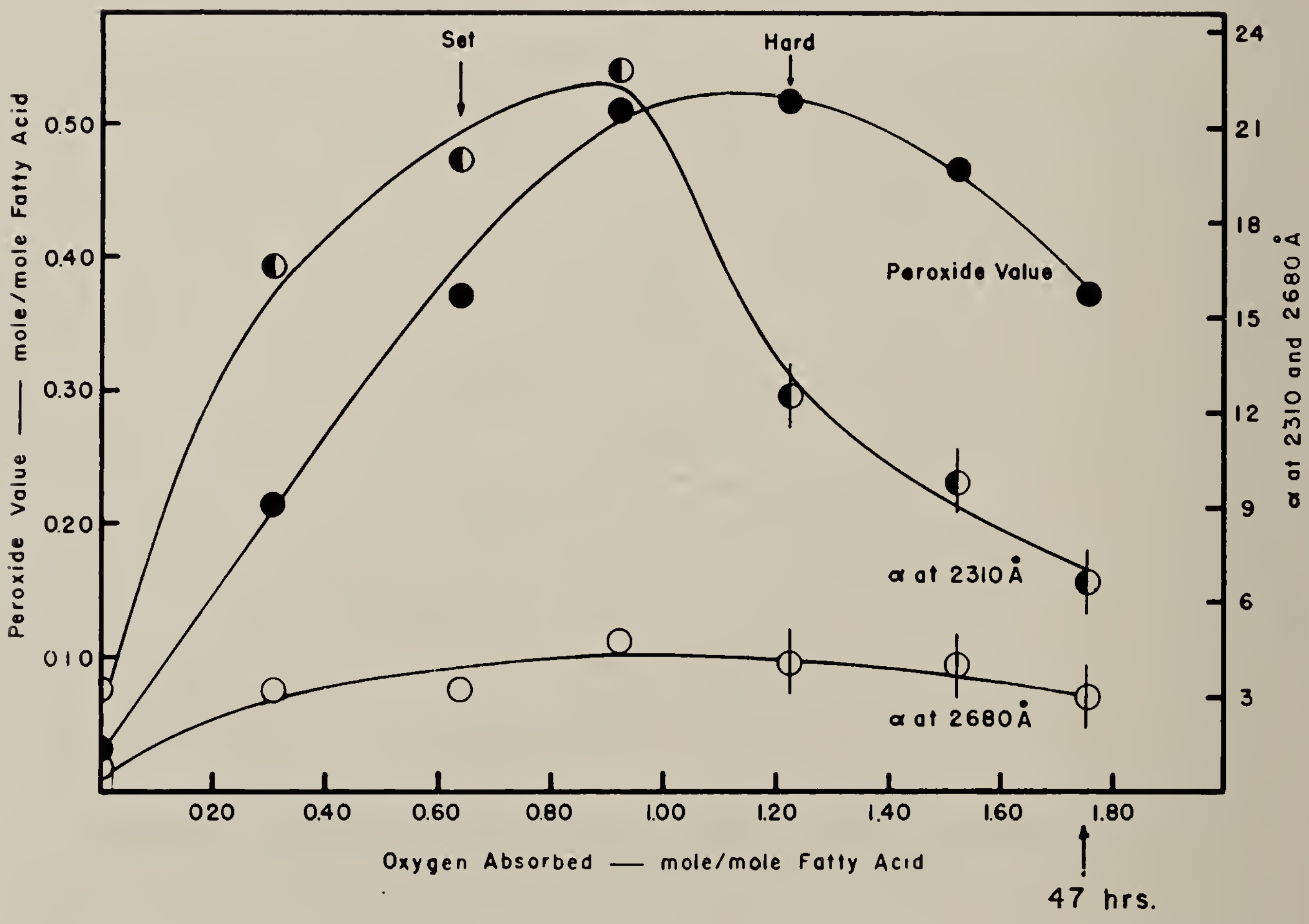

Fig. XIII-9. Changes in peroxide value and UV spectra of oxidizing PE linoleate films.

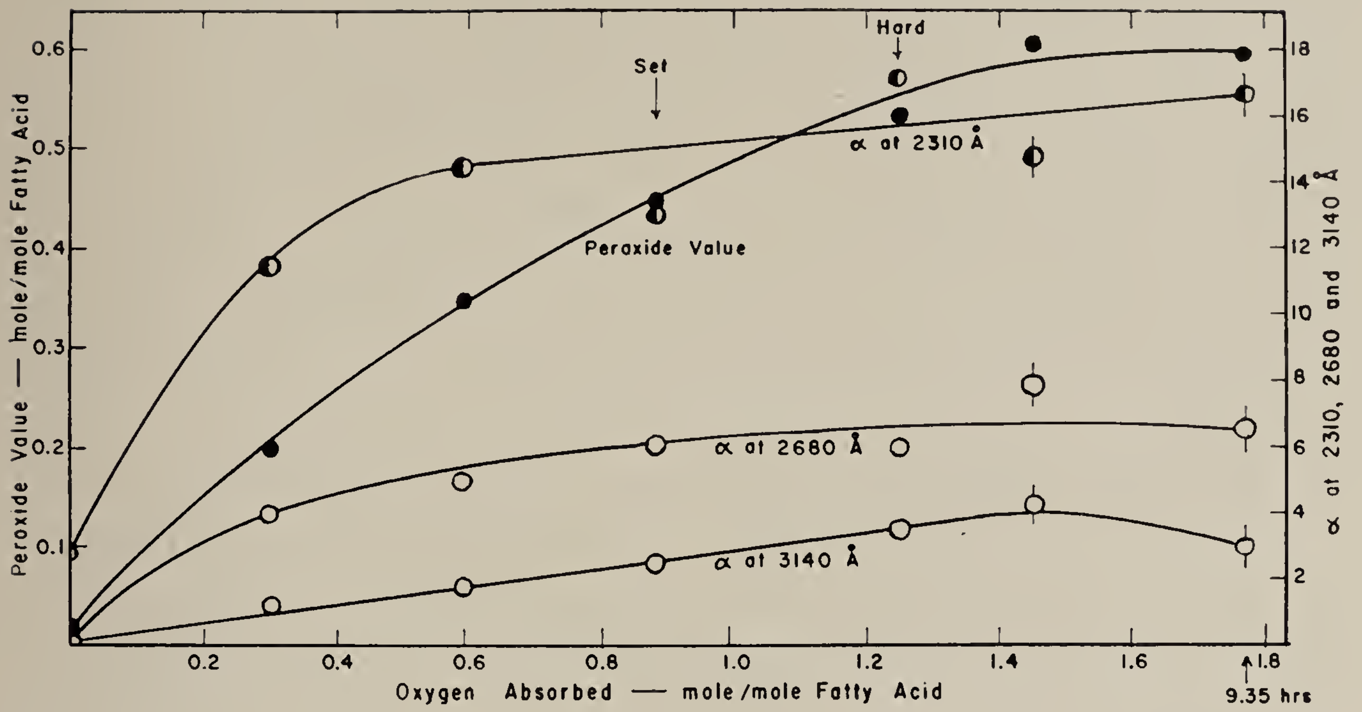

Fig. XIII-10. Changes in peroxide value and UV spectra of oxidizing PE linolenate films.

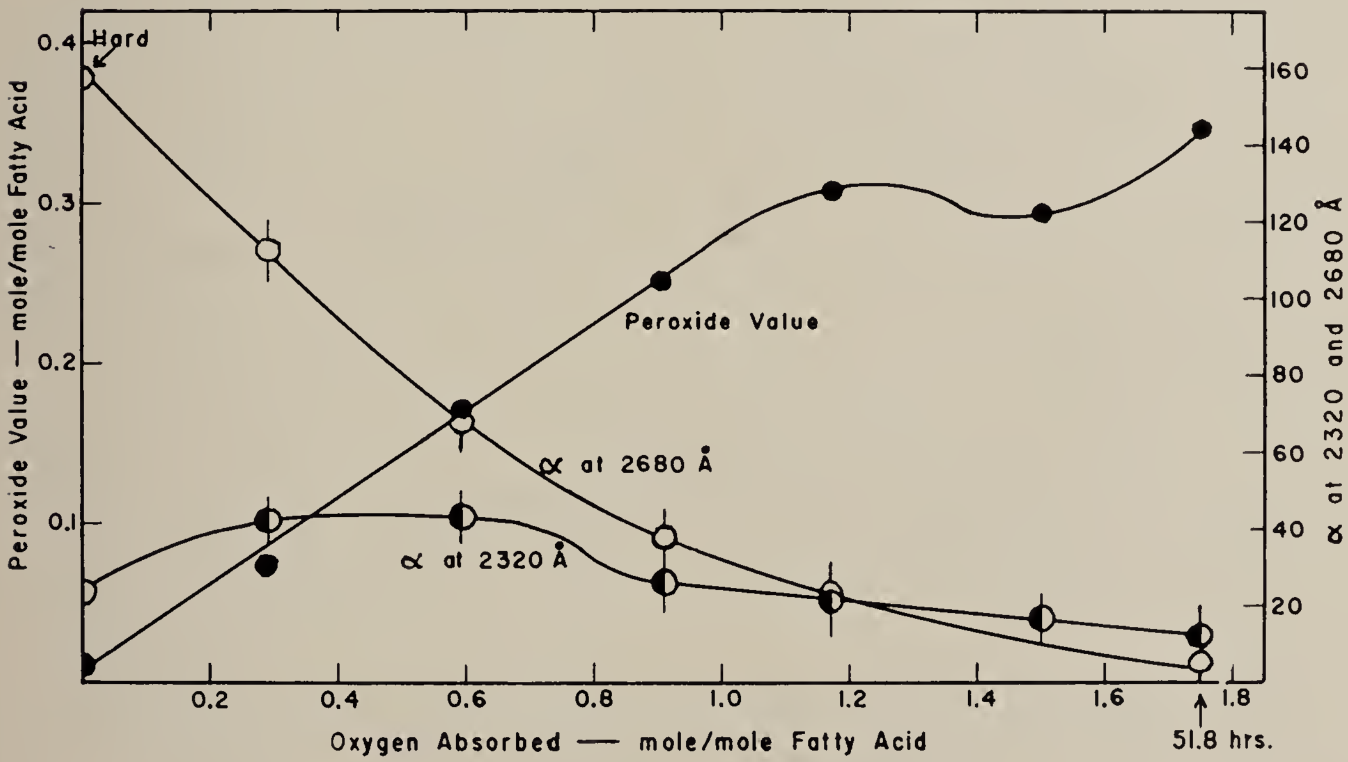

Fig. XIII-11. Changes in peroxide value and UV spectra of oxidizing PE eleostearate films.

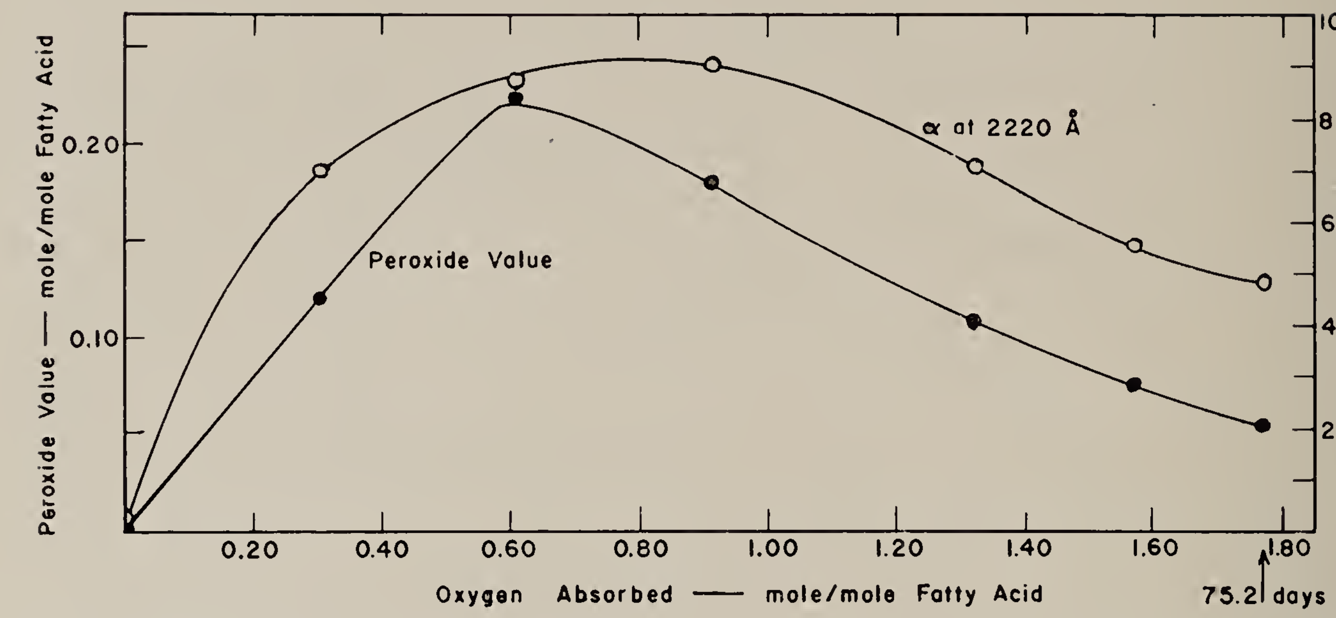

Fig. XIII-12. Changes in peroxide value and UV spectra of oxidizing diPE oleate films.

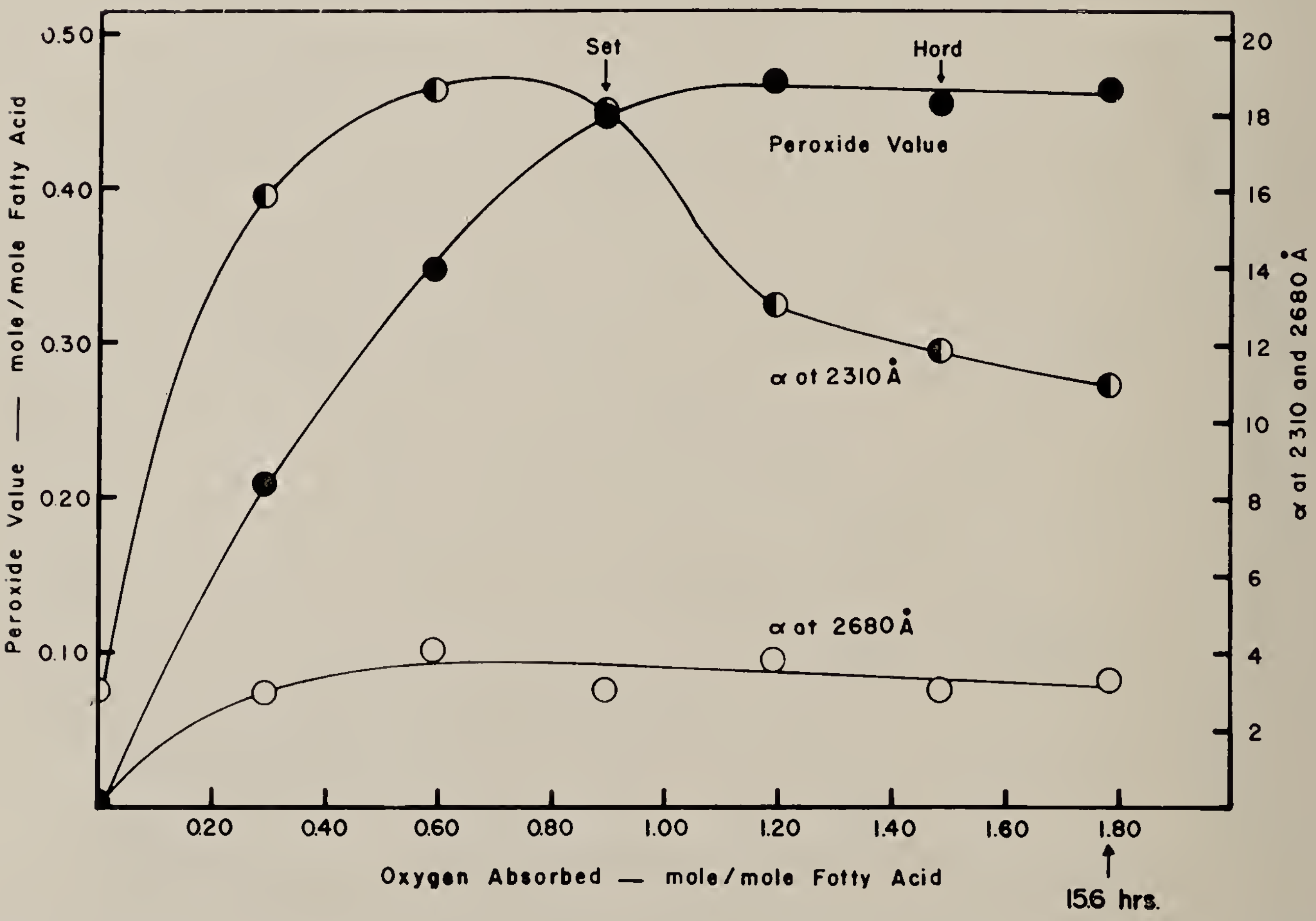

Fig. XIII-13. Changes in peroxide value and UV spectra of oxidizing diPE linoleate films.

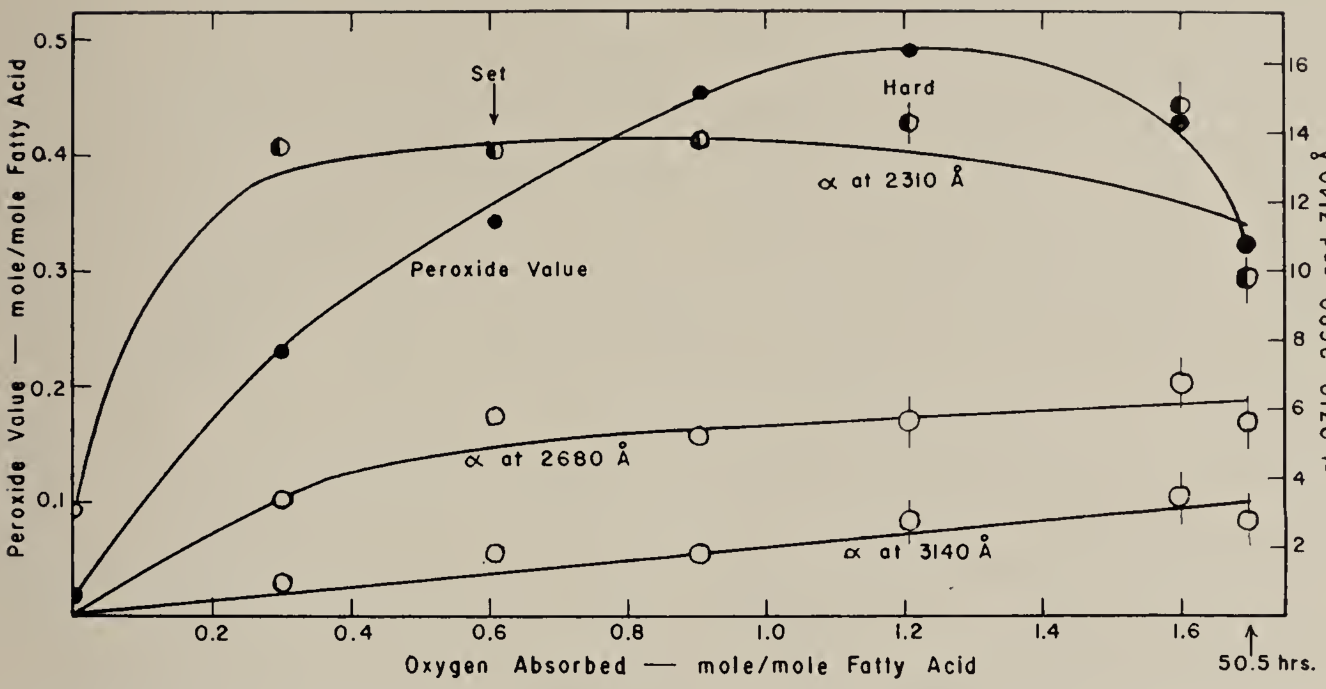

Fig. XIII-14. Changes in peroxide value and UV spectra of oxidizing diPE linolenate films.

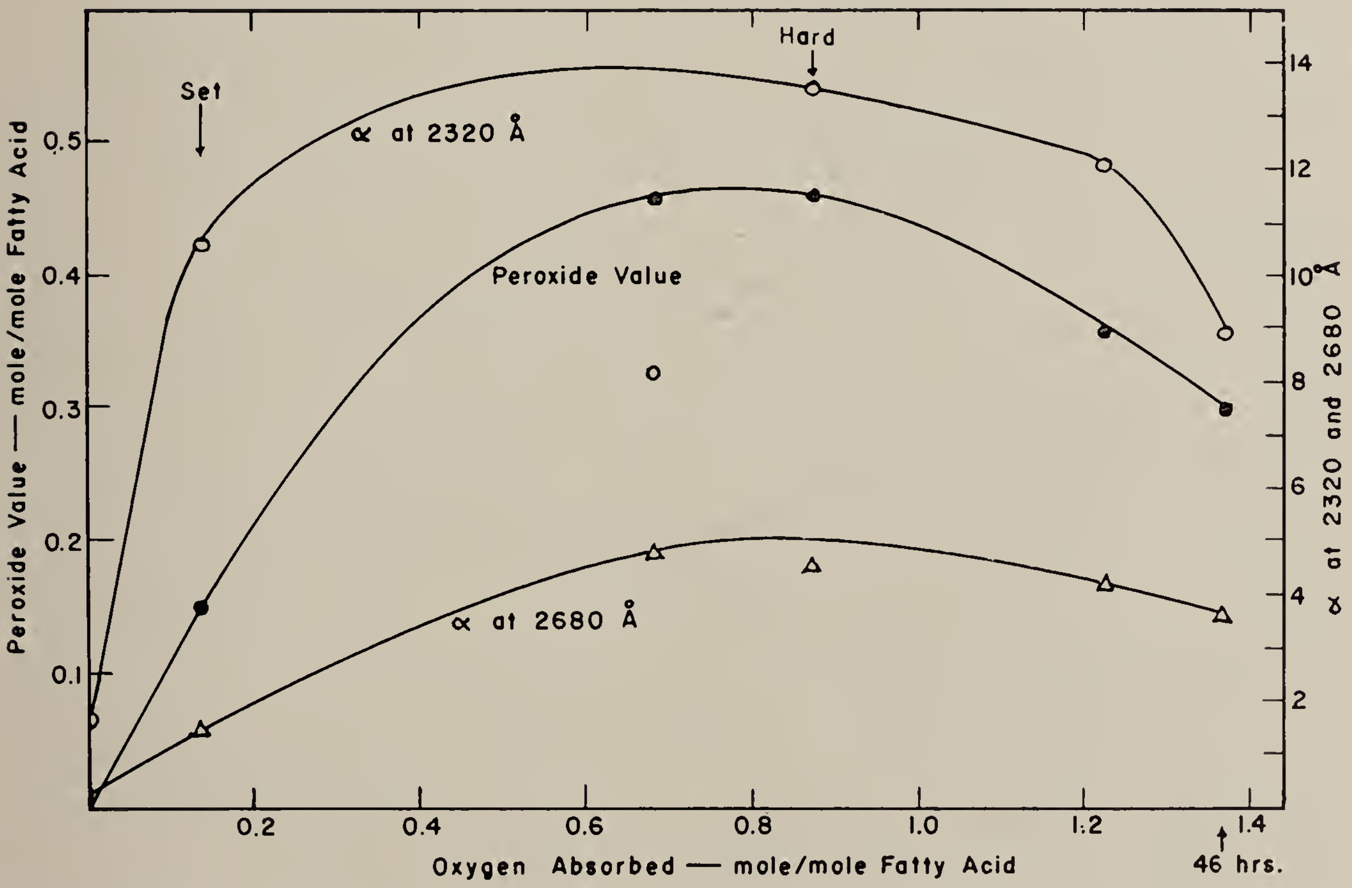

Fig. XIII-15. Changes in peroxide value and UV spectra of oxidizing LO linoleic glycerol alkyd films.

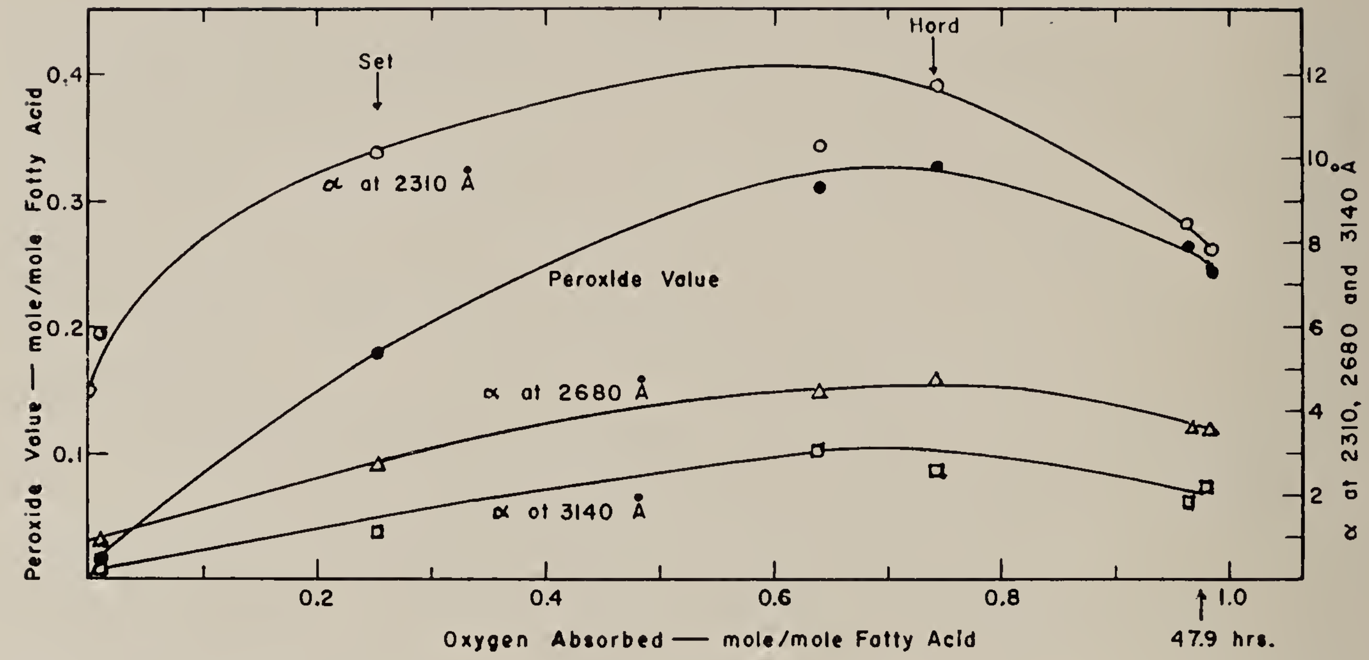

Fig. XIII-16. Changes in peroxide value and UV spectra of oxidizing LO linolenic glycerol alkyd films.

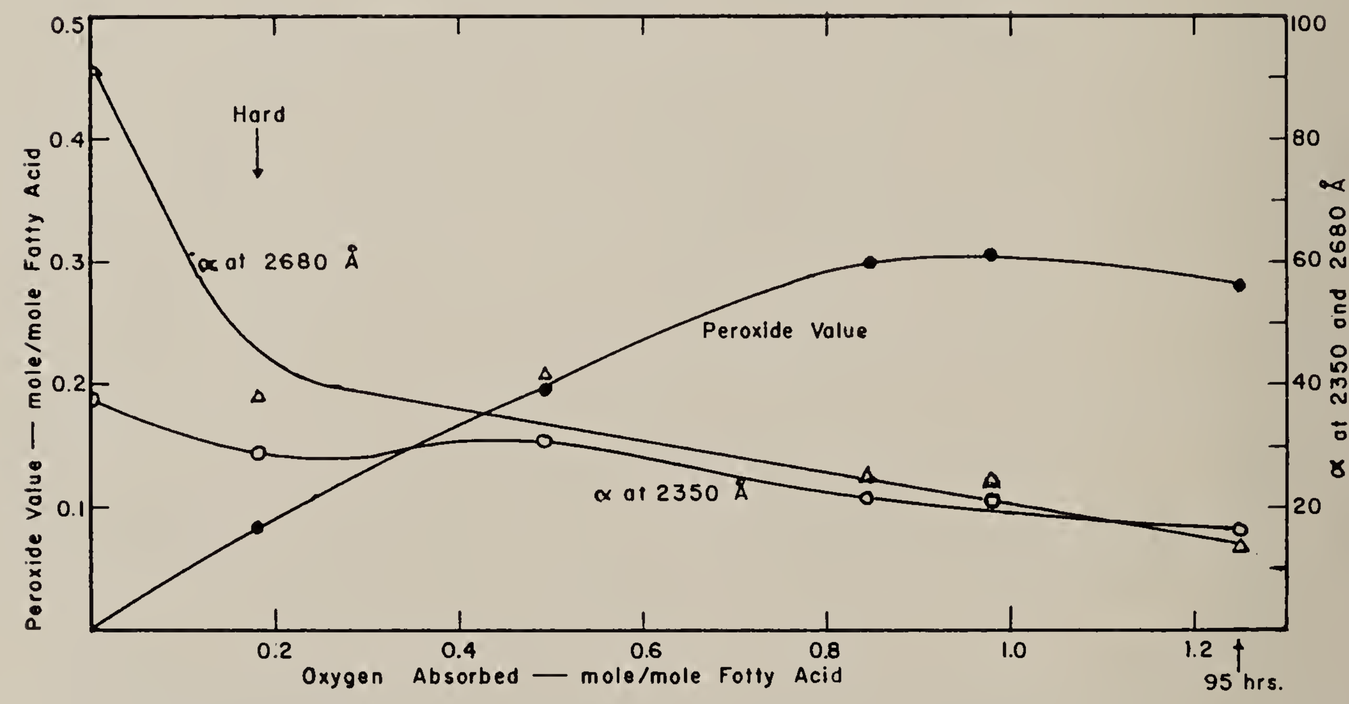

Fig. XIII-17. Changes in peroxide value and UV spectra of oxidizing LO eleostearic glycerol alkyd films.

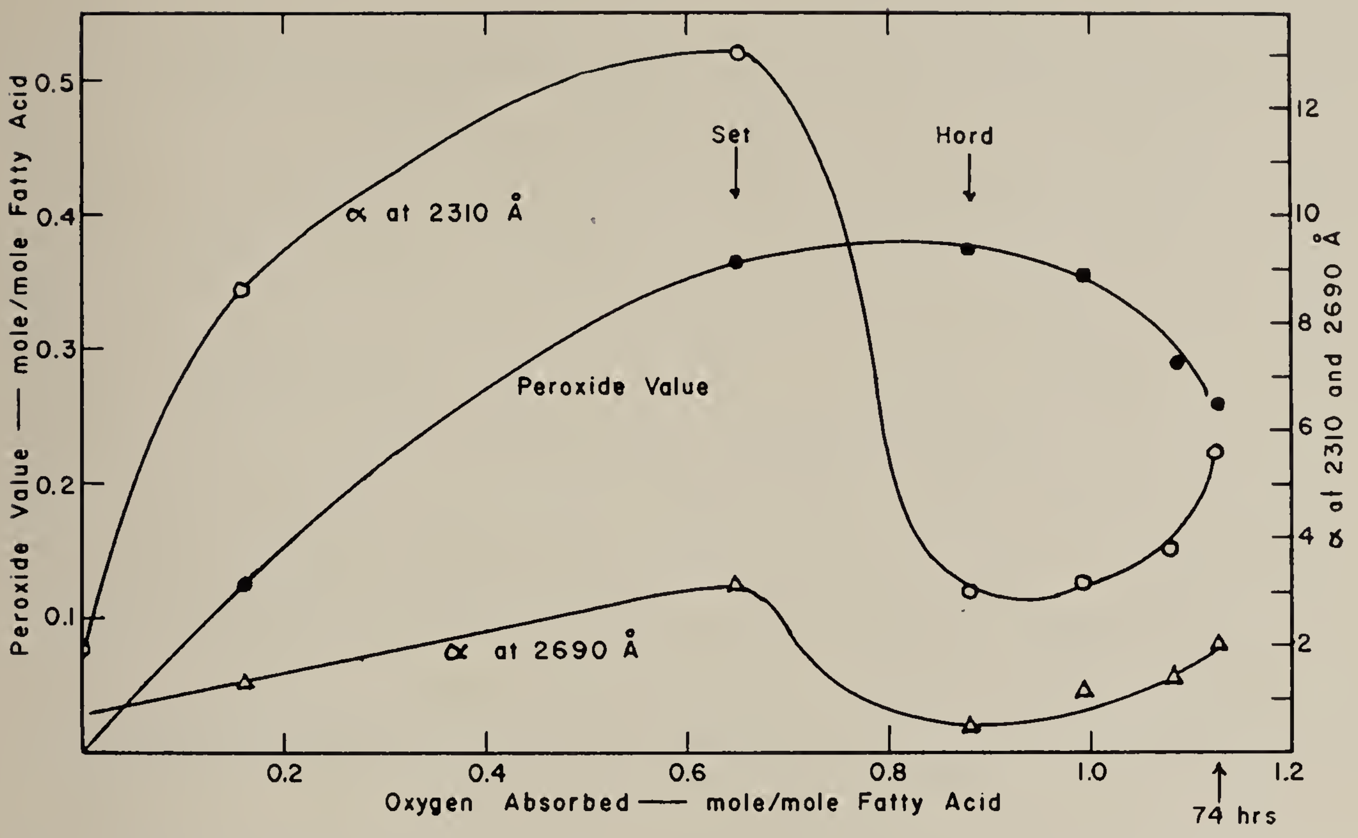

Fig. XIII-18. Changes in peroxide value and UV spectra of oxidizing SO linoleic glycerol alkyd films.

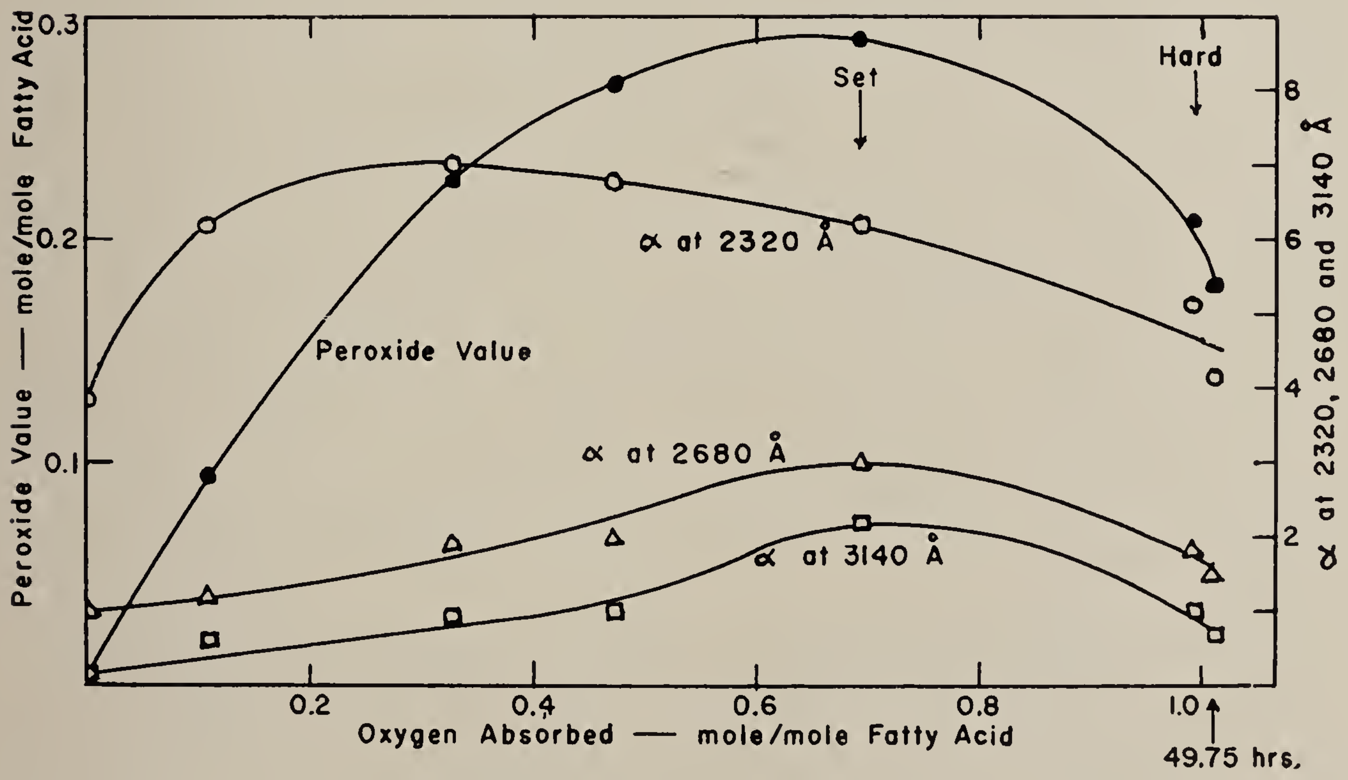

Fig. XIII-19. Changes in peroxide value and UV spectra of oxidizing SO linolenic glycerol alkyd films.

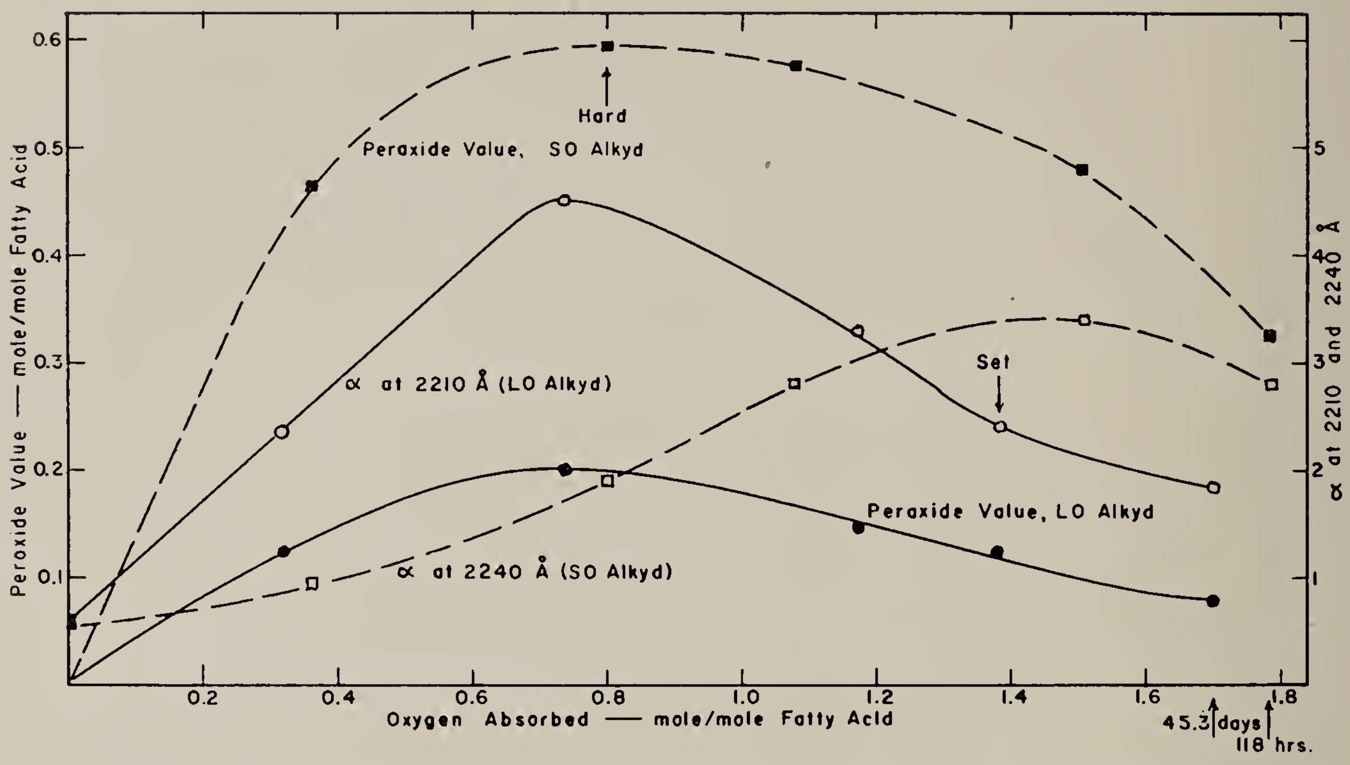

Fig. XIII-20. Changes in peroxide value and UV spectra of oxidizing LO and SO oleic PE alkyd films.

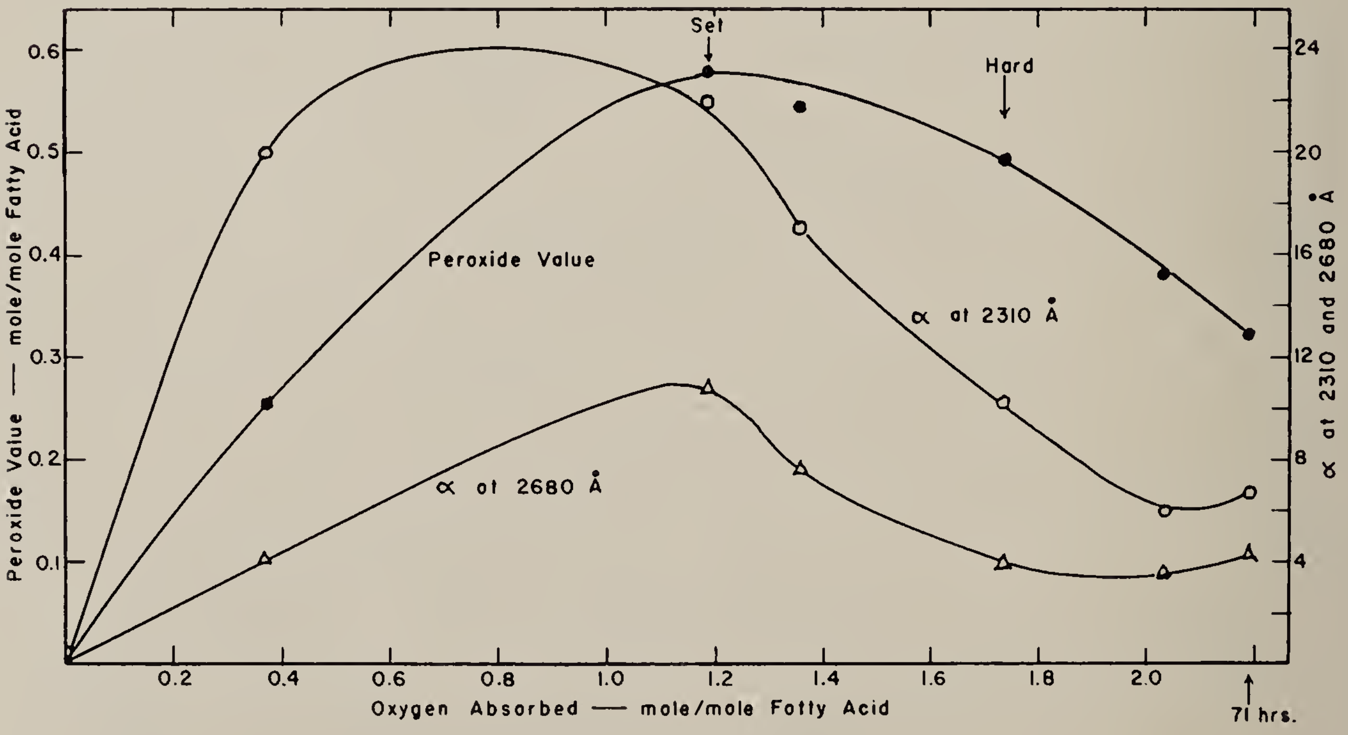

Fig. XIII-21. Changes in peroxide value and UV spectra of oxidizing LO linoleic PE alkyd films.

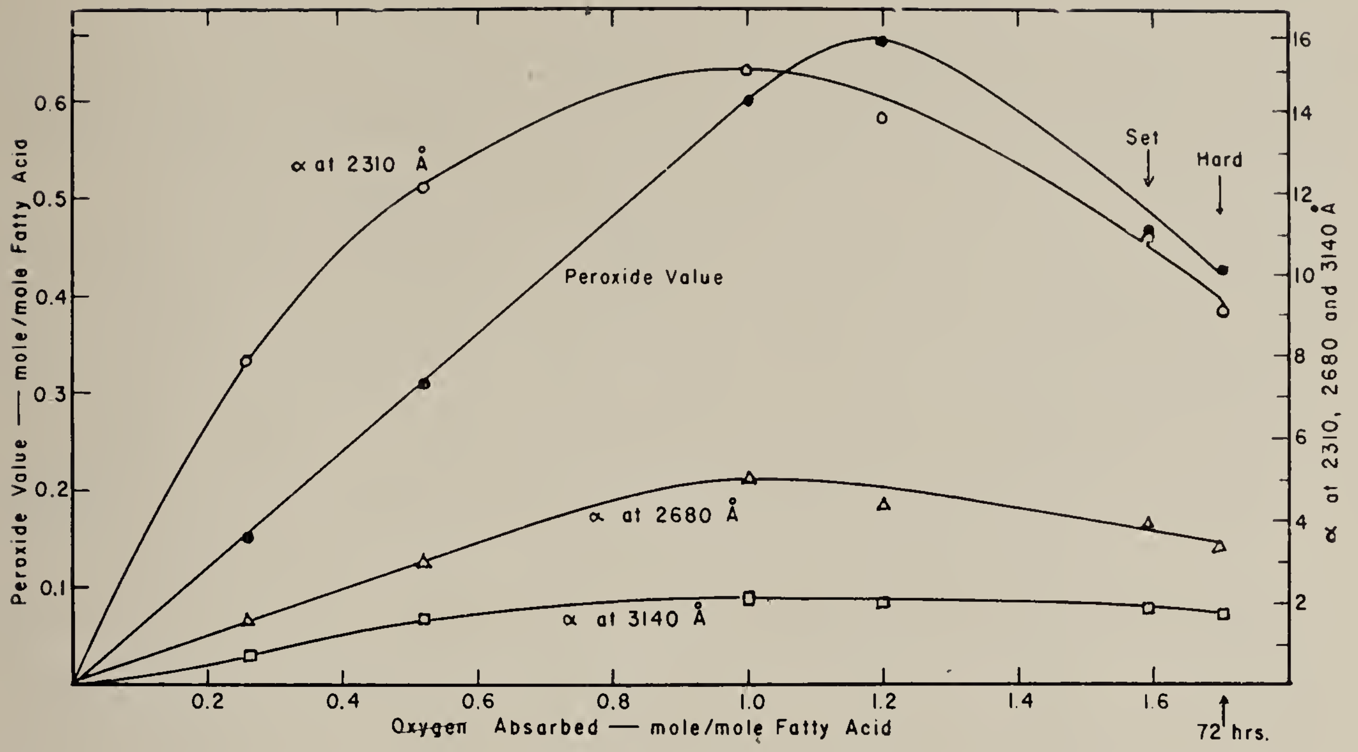

Fig. XIII-22. Changes in peroxide value and UV spectra of oxidizing LO linolenic PE alkyd films.

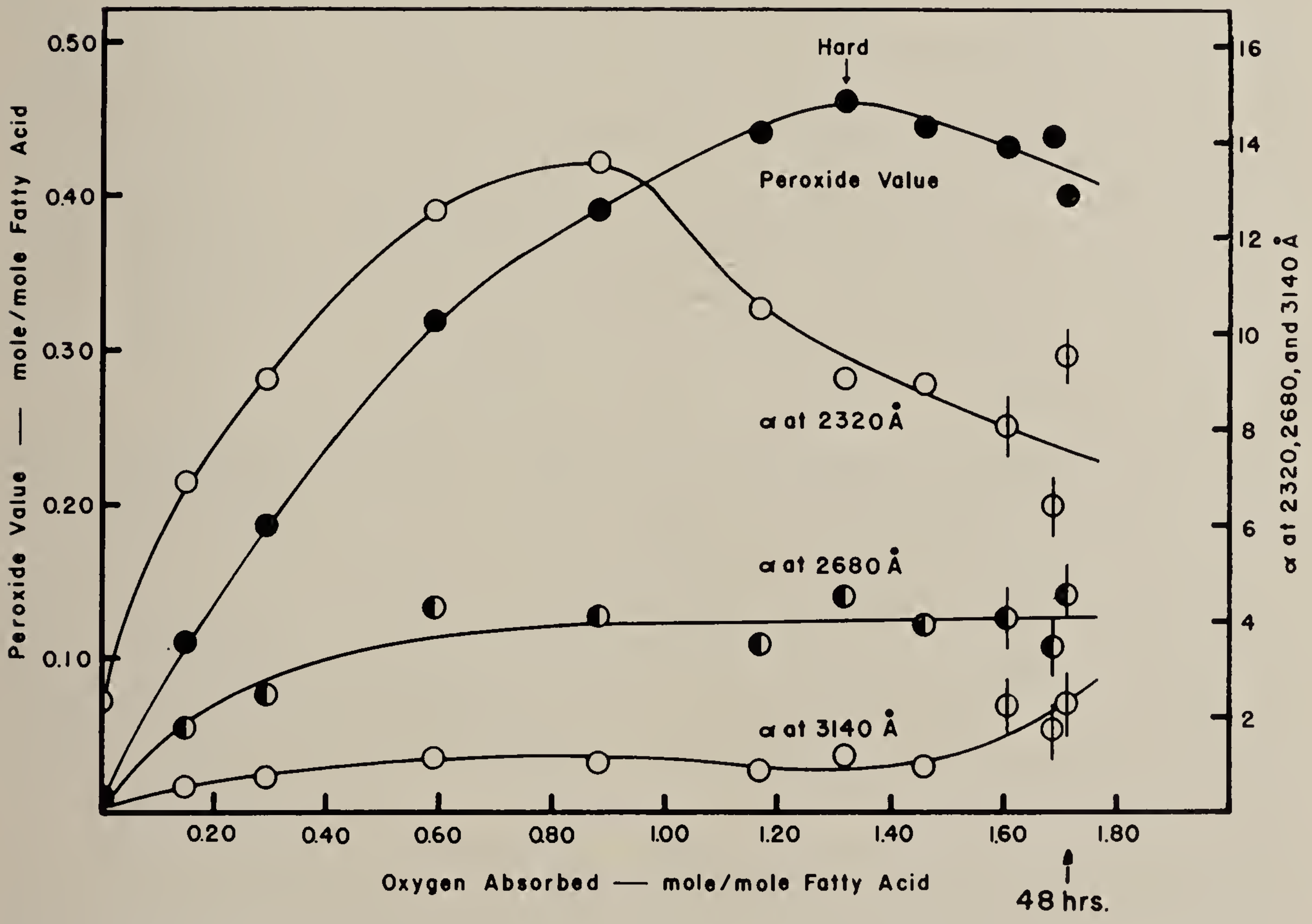

Fig. XIII-23. Changes in peroxide value and UV spectra of oxidizing varnish linseed castor oil films.

follows oxygen absorption is always expressed in those terms. In all cases, when oxidation was continued long enough, the peroxide content reached a maximum and began to decrease. Table XIII-2 presents the ratios of peroxide values to oxygen absorbed at an absorption level of 0.3 mole per mole of fatty acid, and the age at the maximum peroxide value. The oxygen absorption levels at which the films were "set" and "hard," the maximum peroxide values attained, and the corresponding oxygen absorptions, all expressed in moles per mole of fatty acid, are also given.

In the case of the SO oleic PE alkyd, an erroneous value of 1.35 for P.V./O_2 is due to experimental error of unknown origin (possibly a leak) at least in the first measurement and perhaps in the others; there is no way to be sure.

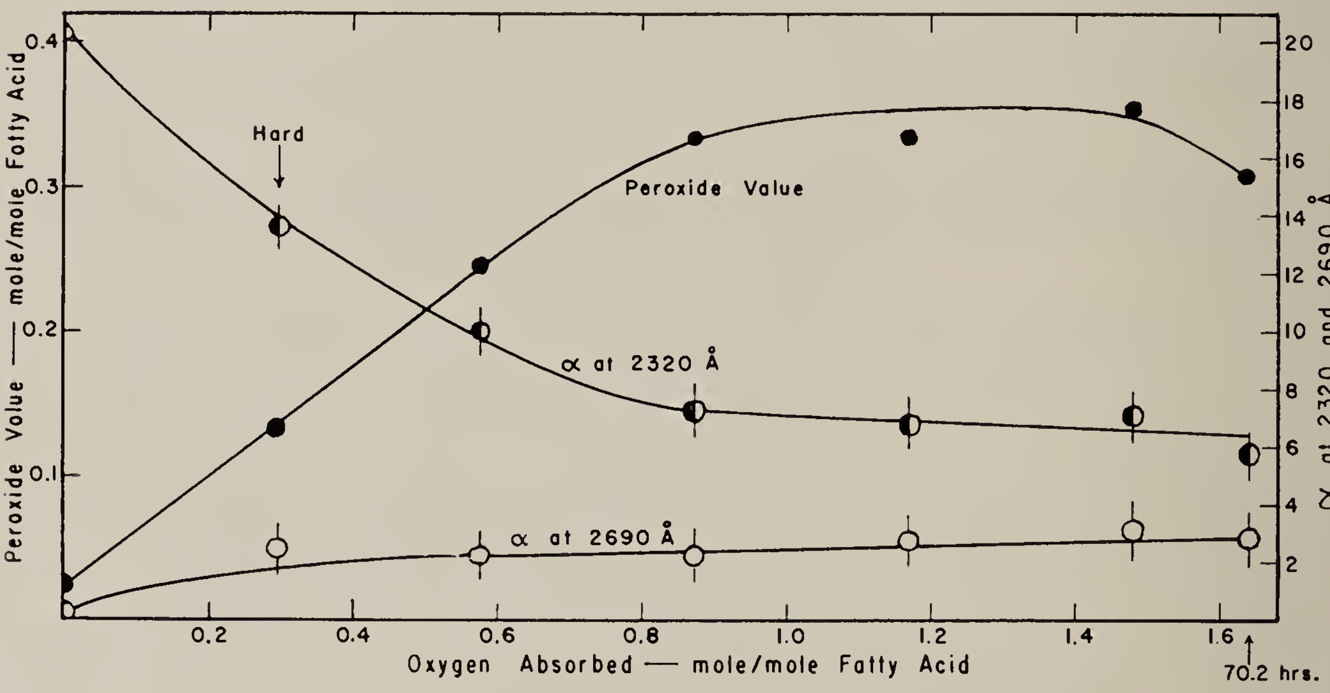

Fig. XIII-24. Changes in peroxide value and UV spectra of oxidizing dehydrated castor oil films.

Oleate esters. PE and diPE oleates (Figs XIII-8 and XIII-12), following similar patterns, accumulated peroxides in almost direct proportion to oxygen absorption, but a little less than half of that oxygen appeared in peroxide form. Beyond the 0.6 mole oxygen absorption level, the ratio of peroxides to oxygen absorbed fell off rapidly as peroxide accumulation reached a maximum. The compounds developed spectral absorption in the region of 2200 Å, with intensity rising slightly faster and to an earlier maximum than peroxide value. Neither compound dried.

TABLE XIII-2

Oxidation of Films of Pure Compounds

(Values in columns 2, 3, 5, and 6 expressed in terms of moles per mole of fatty acid)

Compound	P.V./O_2 absorbed at 0.3 mole O_2/mole F.A. (1)	O_2 absorbed when film was		Time to reach max. P.V. (hr.) (4)	Max. P.V. attained (5)	O_2 absorbed at max. P.V. (6)
		Set (2)	Hard (3)			
Trilinolein	0.69	1.17	—	8.4	0.53	1.26
Trilinolenin	0.65	1.46	—	2.6	0.55	1.35
Trieleostearin	0.29	—	0.29	14.0	0.37	1.47
PE oleate	0.47	—	—	375	0.25	0.83
PE linoleate	0.71	0.89	1.48	5.6	0.47	1.13
PE linolenate	0.63	0.88	1.26	4.5	0.61	1.58
PE eleostearate	0.28	—	0.29	18.0	0.31	1.20
DiPE oleate	0.42	—	—	312	0.23	0.68
DiPE linoleate	0.52	0.64	1.22	5.2	0.52	1.11
DiPE linolenate	0.70	—	0.61	5.4	0.51	1.28
				(min.)		
LO linoleic glycerol alkyd	0.95	0.14	0.87	6.2	0.47	0.77
LO linolenic glycerol alkyd	0.67	0.26	0.74	6.0	0.34	0.75
LO eleostearic glycerol alkyd	0.43	—	0.18	46	0.30	0.95
SO linoleic glycerol alkyd	0.74	0.65	0.87	9.5	0.38	0.82
SO linolenic glycerol alkyd	0.71	0.69	0.99	4.5	0.29	0.68
LO oleic PE alkyd	0.41	1.39	—	190	0.20	0.76
LO linoleic PE alkyd	0.75	1.19	1.72	5.0	0.57	1.24
LO linolenic PE alkyd	0.63	1.59	1.70	7.0	0.65	1.17
SO oleic PE alkyd	1.35	0.35	0.80	80	0.60	0.83
Varnish linseed oil	0.62	—	1.32	408	0.46	1.31
Dehydrated castor oil	0.45	—	0.30	870	0.35	1.20

Linoleate esters. Trilinolein, PE linoleate, and diPE linoleate (Figs. XIII-5, XIII-9, and XIII-13), allowed to oxidize to a level of 1.8 mole O_2, exhibited similar curves; however, the ratio P.V./O_2 absorbed for the diPE ester was definitely lower, and the decrease of peroxide content beyond the maximum faster, than for the other two. Perhaps this was, at least partly, because diPE linoleate absorbed oxygen more slowly, after reaching the level of 1.5 mole, than the other two compounds, which continued at nearly their original rate.

The spectral absorption developed in the conjugated diene region (2312 to 2320 Å) was much the same for all three compounds. When 0.3 mole O_2 had been absorbed, approximately 74% of the peroxides were conjugated diene peroxides. Beyond this point the accumulation of conjugated diene fell off rapidly, particularly for PE linoleate. Diene absorption reached a maximum shortly ahead of maximum peroxide value; highest for the triglyceride, lowest for the pentaerythrityl ester. All three compounds developed about the same small amounts of triene.

Functionality of alcohol was indirectly related to oxygen uptake at the setting point, which was 0.6, 0.9, and 1.2 moles per mole acid for diPE, PE, and glyceryl esters, respectively. Trilinolein, however, did not reach the "hard" state during the course of the experiment. PE linoleate was "hard" at a level of 1.5 mole O_2, but the film still remained soluble in the chloroform-acetic acid solvent, and the reduced material was soluble in ether. For diPE linoleate, the films were hard at 1.2 moles O_2; they were insoluble and had to be saponified for spectral measurements.

Linolenate esters. The oxidation proceeded with these (Figs. XIII-6, XIII-10, and XIII-14) in similar fashion to the linoleates, but at somewhat higher initial rates. After 1 mole of oxygen had been absorbed, diPE linolenate slowed appreciably; and it slowed almost to a stop beyond 1.6 moles. The ratio of peroxide accumulation to oxygen absorption stayed at about the same level during the early stages as with the linoleates. Similar maximum peroxide contents were attained but at somewhat higher oxygen absorption levels. Conjugated diene content (as measured by spectral absorption) built up more slowly than for linoleates; its ratio to peroxide value was only about half as much at the start. Some triene and tetraene absorption developed as oxidation progressed. Trilinolenin did not appear set until 1.46 moles O_2 had been absorbed, and had not reached the hard stage when the experiment was stopped at an oxygen absorption in excess of 2 moles. The films of PE and diPE linolenates were "set" and "hard" at approximately the same absorption levels as for the corresponding linoleate esters.

Eleostearate esters. With both trieleostearin and PE eleostearate (Figs. XIII-7, XIII-11), peroxide content increased in direct proportion to oxygen absorbed until a maximum had been nearly reached, but only 30% of that oxygen appeared as peroxides measurable by the iodimetric method. After reaching a maximum, the measured peroxide content dropped but later tended upward again. Destruction of triene with respect to oxygen uptake was quite constant at a ratio of 3 moles of triene lost for 4 moles of oxygen absorbed up to an absorption level of 0.9 mole; it fell off beyond this point. The eleostearate films set rapidly; all samples were hard and insoluble in the solvent used for peroxide analyses. The reduced films, also insoluble, had to be saponified for spectral measurements.

Varnish linseed oil. This followed a pattern (Fig. XIII-23) similar to that of diPE linolenate. Maximum peroxide content and extent of diene, triene, and tetraene conjugation were all less than for the pure linolenate esters because of the diluting effect of the more saturated fatty acids present in linseed oil. Nevertheless the films dried at lower oxidation levels than trilinolenin. They were hard when 1.32 moles of oxygen had been absorbed. Samples tested at lower oxidation levels, although very viscous and tacky, did not appear set according to the criterion established.

Dehydrated castor oil. This oil, characterized like the eleostearates by conjugated unsaturation, resembled them also in oxidation behavior. Until absorption reached 0.6 mole, about 45% of the oxygen uptake appeared as peroxides; the proportion then decreased rapidly, and a maximum peroxide value was reached at 1.2 moles (Fig. XIII-24). The diene conjugation fell off rapidly at first, then became more nearly constant. Dry, insoluble films formed quickly.

Alkyds in general. Except with the LO eleostearic glycerol alkyd and the long-oil PE alkyds of linoleic and linolenic acids, peroxide values reached their maxima at remarkably similar levels of oxygen absorption, 0.7 to 0.8 mole. This point fell, in several cases, close to that at which the films were first observed to be "hard." Curiously enough, the long-oil alkyds of the tetrafunctional alcohol pentaerythritol did not "set" or "harden," and did not reach peroxide maxima, until much more oxygen had been absorbed than was required to bring the other compounds to similar states.

Oleic alkyds. The short-oil PE compound (Fig. XIII-20) attained a much higher peroxide value than the long-oil alkyd. The spectral absorptions recorded at 2210 Å do not represent an absorption peak; instead, they are measurements made at the lower wavelength limit of the instrument, and they are on one slope of an absorption peak existing at some wavelength below 2210 Å. With the long-oil alkyd, changes in UV absorption closely paralleled peroxide values. The probable error in some measurements, mentioned above, may explain why results with the short-oil alkyd differed. The short-oil compound dried hard; the long-oil did not.

Linoleic alkyds. Peroxide values and spectral absorption in the conjugated diene and triene regions rose to a maximum, then fell off. For the LO glycerol alkyd (Fig. XIII-15) all three maxima were reached at the same oxygen uptake level and subsequent decrease in conjugation was slow. The film set before the maxima were reached and was "hard" shortly after. The conjugated diene and triene in the SO glycerol (Fig. XIII-18) and LO PE (Fig. XIII-21) alkyds reached their top value before peroxide maxima occurred; they decreased rapidly then but tended upward at the final measurements. At the stage of 0.3 mole oxygen absorption, the fatty acid peroxides in the long- and short-oil glycerol alkyds appeared to contain about the same amounts of conjugated diene, but much less than the LO PE alkyd peroxides.

Linolenic alkyds. The long-oil (Fig. XIII-16) and short-oil (Fig. XIII-19) glycerol compounds developed peroxides at similar rates and to about the same maximum values. The long-oil PE resin (Fig. XIII-22), though slower in attaining maximum peroxide value (only at the 1.2 moles oxygen level), pushed it twice as high as for the other two linolenic alkyds. Diene absorption curves had different shapes; for the short-oil (glycerol) resin the maximum came early, was rather low, and was followed by slow decrease. For the others, maxima came later and were higher, and the decrease was more rapid. Both glycerol alkyds exhibited appreciable diene absorption before oxidation began; small amounts of triene and tetraene absorption developed later. All three resins dried to "hard" films, but the pentaerythritol alkyd took more oxygen and more time to reach this stage.

Eleostearic alkyds. Since the SO glycerol alkyd of this fatty acid had gelled in the sealed ampules, only the long-oil compound (Fig. XII-17) could be studied. As oxygen up to about 0.2 mole was taken up, triene conjugation fell off rapidly at first, slowly from then on. Diene conjugation decreased as a straight-line function of oxygen absorption throughout the experiment. The original triene absorption of the fatty acids recovered from the unoxidized alkyd was low ($a = 90$) and the diene high ($a = 38$). For both trieleostearin and PE eleostearate these values for diene and triene absorption correspond to an oxidation level of approximately 0.5 mole, and actually the curves for changes in diene, triene, and peroxide values of the eleostearic alkyd are very similar to that part of the trieleostearin curves at oxidation levels above that figure. It appears likely that this alkyd was oxidized to some extent before any of the measurements were begun. Since the control sample had only an insignificant peroxide value (10 meq. per kilogram) it may be that this compound became somewhat oxidized during preparation and that the peroxides decomposed either before or during storage.

Second Phase: Detailed Studies of Trilinolein and Trilinolenin

In this second phase of the oxidation studies, Chipault and McMeans employed much larger film areas of trilinolein and trilinolenin. They collected them at two levels of oxidation, and after determining peroxides, they reduced and saponified the remainder of the films. They analyzed for hydroxyl, alpha glycolic, and carbonyl content, measured the unsaturation of the free acids, and determined the neutralization equivalent, molecular weight, and ultraviolet and infrared spectral characteristics of these acids.

Preparation of Films

Samples of about 12.5 grams of triglyceride were transferred to nitrogen-filled test tubes, mixed with drier, and aged in the manner described earlier in this chapter. Then 11.62 grams of material was brushed uniformly on a glass plate 61.5 × 64 cm., giving a film the mean thickness of which was about 1.25 mils. The plate was set in a cabinet where it was illuminated at prescribed intensity, and where standard temperature and humidity were maintained as closely as possible. Some of the experiments had to contend with hot, humid summer weather and exact control in the cabinet was impossible. Actual conditions of oxidation for each film are shown in Table XIII-3.

TABLE XIII-3. Analysis of Reduced Fatty Acids of Oxidized Films

		Trilinolein					Trilinolenin			
		Film 1		Film 2			Film 1		Film 2	
	Linoleic acid, theory	Tacky	Tack-free	Tacky	Tack-free	Linolenic acid, theory	Tacky	Tack-free	Tacky	Tack-free
Drying conditions										
Temperature (°F.)		73	73	73	73		80	80	74	74
Humidity (relative)		61	61	58	58		72	72	55	55
Exposure time (hr.)		12	13	11.25	12		2.5	3.0	3.25	4.0
Analytical values*										
Peroxide content (moles/kg.)	0	1.77	1.56	1.66	1.85	0	Film lost	1.09	1.29	1.42
Hydroxyl content (moles/kg.)	0	2.55	2.55	†	†	0	—	†	†	†
Alpha glycolic group (moles/kg.)	0	1.09	1.02	0.97	0.96	0	—	0.91	0.78	0.75
Unsaturation (double bonds/kg.)	7.13	4.23	3.62	4.16	3.69	10.08	—	5.40	5.69	5.48
Unsaturation (double bonds/mole)	2	1.16	0.96	1.06	0.91	3	—	1.70	1.47	1.25
Carbonyl other than —COOH (moles/kg.)	0	0.77	0.75	0.61	0.45	0	—	0.77	0.69	0.48
Neutralization equivalent	280.4	276.7	280.1	290.8	292.7	278.4	—	283.6	275.6	276.3
Molecular weight	280.4	273.0	262.8	251.8	244.3	278.4	—	320.3	245.1	233.1
		276.7	265.9	249.2	249.1		—	317.3	256.5	222.2
Specific alpha at 2320 A	1.25‡	25.9	21.6	26.5	26.1	1.63‡	—	18.4	20.1	20.5
Specific alpha at 2700 A	0.21‡	4.21	4.02	3.58	3.70	0.31‡	—	8.42	10.08	21.7

* Peroxides were determined on oxidized films; all other values are on the acids obtained by saponification of the reduced films. † See Table XIII-4. ‡Calculated from values obtained on the unoxidized triglycerides.

The films were frequently tested by touch. Efforts were made to remove half of each film when it first became tacky and the other half when it had just lost its tack but was still soft and easily scratched.

The films were scraped from the glass with a razor blade. The scrapings of the first sample promptly ignited spontaneously when accumulated in a small flask. For the other samples, therefore, a small portion of film was removed for peroxide determination and the rest of it was placed directly in about 400 ml. of dioxane through which oxygen-free nitrogen was bubbling. The portion of film gathered with each stroke of the blade was dropped into the solvent so that no large amounts of the rapidly oxidizing material remained in dry state.

Preparation of Reduced Acids

The amount of film gathered from each sample was estimated to be about 5.7 grams, and the quantity of stannous chloride required to reduce it was calculated from the peroxide value. Five times this quantity of stannous chloride, dissolved in 30 ml. of 95% alcohol, was added to the dioxane suspension of film. The film dissolved completely, and reduction was allowed to proceed for 16 hours at room temperature under nitrogen. At the end of this time 200 ml. of ethyl ether were added and the solution was washed five times with 300-ml. portions of 0.5 *N* HCl in air-free water, then with water until neutral. The ether solution was dried over sodium sulfate and the solvent evaporated under vacuum. The reduced material was saponified, acidified, and extracted with ether; the extract was washed, dried, and evaporated under vacuum to recover fatty acids.

Analytical Methods

Hydroxyl value: determined by the method of Ogg, Porter, and Willits (7). Replicate OH assays on fatty acids from one trilinolein film and both trilinolenin films failed to agree as closely as was desired. The method of Chang and Kummerow (3) was also tried, with no better agreement. These values are given separately in Table XIII-4.

Alpha glycolic content: periodic acid method of Pohle and Mehlenbacher (8).

TABLE XIII-4

Hydroxyl Contents of Reduced Acids from Oxidized Films

(Moles per kilogram)

	Method	
	Ogg, Porter & Willits	Chang & Kummerow
Trilinolein film 2		
Tacky	2.77, 2.38	4.42, 4.24
Tack-free	2.88	2.73, 3.08
Trilinolenin film 1		
Tack-free	2.58, 2.49	—
Trilinolenin film 2		
Tacky	1.87, 2.78, 2.72, 3.47	2.62, 3.15
Tack-free	2.51, 2.93, 2.59, 3.07	2.68, 3.42

Iodine value: Woburn method (9).

Neutralization equivalent: by titration with standard alkali.

Carbonyl value: method of Findley and Brown (4) using as solvent 30 ml. absolute ethanol and 5 ml. toluene.

Peroxide value: iodimetric method in the absence of air (5).

Ultraviolet spectral measurements: with a Beckman Model DU spectrophotometer in regions of conjugated diene and triene absorption.

Infrared measurements: on liquid films of the recovered fatty acids with a Perkin Elmer Model 21 double-beam spectrophotometer.

Molecular weight: cryoscopic method using cyclohexanol as solvent (6). Eastman's cyclohexanol was redistilled in a Podbielniak Hypercal column and the fraction with a melting point of 24.8° C. or higher was collected. In using cyclohexanol previously for molecular weight determination, it had been found that its melting point fell appreciably over a period of several months when it was stored in glass stoppered bottles in a desiccator. This lowering of melting point was accompanied by changes in Raoult's constant, K, used for calculation of molecular weight by the formula: mol. wt. $= Kw\,100/tW$, where w is weight of solute, W is weight of solvent, and t is melting point depression. Cyclohexanol also tended to deteriorate when handled under atmospheric conditions. Accordingly the freshly distilled material was promptly sealed under vacuum in 5-gram portions and stored at $-18°$ C. Under these conditions its molar melting point depression remained constant for eight months. Pure oleic acid was used as standard in determining the value of K;

the relationship between concentration and melting point depression was found to be a straight line and the value of K as calculated, 377. This value agrees with that of Wilson and Heron (10) and was used in calculating the molecular weight of the acids from the oxidized films. Determinations were made at two or more concentrations, and in each case two values are reported.

Results

All analytical data (Table XIII-3) were obtained on duplicate films, but the time at which the film was scraped off and analyzed was based solely on the feel of the film to touch. Since this criterion lacks precision, analytical values for duplicate films were not expected to agree. Other possible reasons for discrepancies in the data are lack of uniformity of oxidation conditions and of changes occurring during reduction and hydrolysis of the films, and shortcomings in the analytical methods employed when applied to materials of this nature.

Peroxide values indicate that trilinolein tack-free film 1 was oxidized beyond the level of maximum peroxide accumulation, although films 2 of both trilinolein and trilinolenin may not have been oxidized beyond that stage.

Although the hydroxyl values are not exact, it is probably safe to assume that the reduced acids from all films have a hydroxyl value between 2.5 and 3 moles per kilogram.

The alpha glycolic values indicate that a large proportion of the OH groups occur in the form of alpha glycolic groups.

Unsaturation and molecular weight decreased as the films passed from tacky to tack-free. If the unsaturation per mole of compound is calculated on the basis of the observed molecular weights in each case, and compared with the double-bond content per mole of the corresponding unoxidized fatty acid, it is seen that the films became tacky when approximately one half of the double bonds had disappeared. In the case of trilinolein about half of the remaining double bonds were conjugated. The decrease in molecular weight, however, must result only from chain scission. So many types of polymerization and chain scission may take place in such oxidized materials that no calculation can be made of the extent to which each of these reactions is responsible for the changes observed.

The infrared spectrophotometric data obtained in this project were presented and discussed in Chapter V with those of the projects devoted solely to such studies.

Discussion and Evaluation

Dr. Lundberg, in reviewing the results of the oxidation studies, called attention to these points:

1. Linoleates in thin films were found (page 321) to oxidize at a rate 120 times as great as that of oleates, whereas the highest ratio reported in the literature for rates in bulk is 25:1. Evidently the relative rates are greatly affected when these materials are oxidized in thin films in the presence of driers. Whereas linolenic esters absorbed oxygen nearly three times as fast as those of linoleic acid, the rates for the alkyds of the two acids were initially almost the same, probably because here the rate of oxygen diffusion took control.

2. The rate of oxidation was found to be independent of the nature of the alcohol up to the time when the film set. Because the alcohols of higher functionality (PE and diPE) induce setting at lower levels of oxidation, the rate fell off faster in their compounds than in those of glycerol. All the evidence indicates that differences in rate beyond the set point are due to a lowered rate of diffusion of oxygen into films that have set, rather than to any direct influence of the alcohol.

3. With all compounds except the eleostearates, a relatively high level of oxidation was attained before setting of the film occurred. The level required to cause setting was, as just noted, dependent in part upon the functionality of the alcohol. With trilinolein and trilinolenin, somewhat more than 1 mole of oxygen per mole of fatty acid was needed; with corresponding PE and diPE esters, less than 1 mole sufficed.

4. No oleate compound formed a set film, even at high levels of oxidation, except the SO oleic PE alkyd, and evidence from this and other projects indicates that its setting was independent of any reaction in the oleic acid chains. In contrast, the eleostearate compounds set very quickly at a low level of absorption.

5. In all cases oxygen absorption was accompanied by a marked accumulation of peroxides. The chemical and spectral data indicate that, except in the case of eleostearates, most of the oxygen was used in formation of hydroperoxides. The driers present and other factors caused appreciable decomposition of these hydroperoxides, in some cases quite rapidly, so that at higher oxidation levels the proportions of absorbed oxygen present as peroxides became progressively smaller. Depending on the compound, the molar ratio of peroxide to absorbed oxygen in the initial stages of oxidation ranged from 0.3 to 0.7 or more.

6. For the linoleates and linolenates, spectral evidence indicated that most if not all of the hydroperoxides contained conjugated diene systems. A relatively large quantity of conjugated diene had developed in all the linoleic and linolenic oils and alkyds at the time the films set.

7. With linoleates, and even more with linolenates, an appreciable amount of spectral absorption characteristic of conjugated triene systems developed during oxidation. On the basis of other studies there is evidence that these chromophores consist in part, possibly mainly, of conjugated diene ketones.

8. Oxidation and film setting of eleostearate compounds were accompanied by a loss of conjugated triene and a gain in conjugated diene. In part, these changes are accounted for by oxidation involving formation of cyclic peroxides; in part, by polymerization.

9. Dehydrated castor oil behaved similarly to the eleostearic compounds; however, no conjugated trienes were initially present, and oxidation and setting were accompanied by a loss of conjugated diene.

10. In the rates of oxidation of the alkyds, various anomalies appeared for which no proved explanation is forthcoming. In general, however, it may be said that lesser amounts of oxygen were usually required to reach the setting points of the films than with the simple esters, and the rate of drying was therefore faster. High proportions of the absorbed oxygen appeared in the form of conjugated diene hydroperoxides.

11. With linoleates and linolenates, maxima in the peroxide accumulation curves and also in those for conjugated diene spectral absorption generally appeared at an early stage in the life of the film, and at approximately the same time for any given compound. Moreover, when a downward trend in peroxide content developed, a corresponding destruction of conjugated diene took place, indicating a close chemical interrelation or interdependency of the two phenomena. More highly functional compounds such as diPE linoleate reached maxima in peroxide and conjugated diene curves only after the films had set; simpler compounds, like trilinolein, set at the time of, or after, these maxima.

12. A high proportion of the derivatives formed during oxidation yielded alpha glycolic groups upon reduction with stannous chloride. Whatever the chemical constitution of these precursors of polyhydroxy compounds might be, they were evidently formed in the peroxide decomposition reactions.

13. The only notable changes in any of the measured values during transition of films from a tacky to a tack-free condition were a slight decrease in degree of unsaturation and also an apparent slight decrease in the average molecular weight of the acid residues. The latter was quite unexpected; formation of secondary products of relatively low molecular weight is the only satisfactory explanation. However, if it is assumed that chain scission occurs at a double bond and produces two molecules averaging about half the molecular weight of the original fatty acid, the difference in molecular weight between the tacky and tack-free films is not enough to account for the decrease in unsaturation solely on the basis of chain rupture. Some unsaturation was therefore evidently lost through polymerization reactions, as might be expected.

14. Infrared data indicated that the oxidized films contained appreciable quantities of hydroxyl and carbonyl compounds. In the cases of trilinolein and trilinolenin, the curves also revealed formation of noticeable proportions of *cis, trans* and *trans, trans* conjugated materials. Isolated *trans* double bonds were also definitely present, suggesting that in some cases one or both of the double bonds of the *cis, trans* or *trans, trans* conjugated systems had participated in a polymerization reaction, producing an isolated *trans* double bond.

Interpretations and Conclusions

The oxidation and oxidative polymerization reactions involved in the drying of films stand out from these studies as even more complex than has generally been supposed. Even the more comprehensive studies on films of trilinolein and trilinolenin failed to provide enough data for a clear picture of film formation mechanisms. The studies demonstrated conclusively, however, that the various simple mechanisms hitherto proposed are largely erroneous.

Additional light on the processes of film formation may be gained by further careful study of the data now available. Meanwhile, a few important points have been clearly established by the oxidation studies, as follows:

1. The conjugated diene systems formed during the initial oxidation of linoleates and linolenates play extremely important roles in the subsequent film hardening. Calculations from the data of this project reveal that at the setting point of linoleate and linolenate esters, approximately two conjugated diene groups per original molecule of oil have disappeared. This evidence, plus the failure to find any significant chemical changes other than a decrease in unsaturation in passing from a tacky to a tack-free film, strongly indicates that the conjugated diene systems take part in polymerization reactions, with direct carbon-to-carbon linkages the main probability.

Observations on the oleates and eleostearates bear out such a conclusion. The oleates did not form conjugated diene systems during oxidation but did form hydroperoxides; hydroperoxide groups appear therefore not to be involved as the principal functional groups in polymerization. In the case of eleostearates, film setting requires only a touch of oxidation; the conjugated systems are already present, and apparently the only function of the oxidation is to provide a small amount of peroxides to catalyze their polymerization. Thus, from several points of view, conjugated systems formed during the oxidation of nonconjugated esters of polyunsaturated acids are seen to play a leading role in the drying of the film.

This does not minimize or exclude the importance of secondary reactions governing film characteristics. The mysterious and simultaneous decline in the conjugated diene and peroxide groups, after the conjugated diene curves have reached a maximum, has been mentioned. Whether this in any way involves further polymerization reactions is not known; but there is clear evidence that auxiliary polymerization reactions do occur, with condensation of various secondary products. All these reactions are undoubtedly manifested by effects on chemical and physical properties of the film; hardness, water and alkali resistance, yellowing, and distensibility depend on their nature and extent.

2. The functionality of the special compounds had important relation to the properties studied in other projects. In many of these properties, films of the synthetic oils were found to be inferior to those of ordinary linseed oil and the other commercial vehicles. In general, the Federation compounds were either lower or higher in functionality than commonly used vehicles. The functionality of the oleate compounds was close to 0; that of the trilinolein and trilinolenin was 3, of the corresponding PE esters 4, and of the diPE esters 6. The observations made in project 24 clearly show that these higher functionalities are not needed to produce solid films. The average molecular functionality needed for solid film formation is strongly indicated to be about 2; only a relatively small proportion of molecules of higher functionality than this need be present. An appreciable proportion of molecules of still lower functionality can be present and still lead to satisfactory films.

When the average functionality reaches 3 or more, a considerable amount of oxidation and oxidative degradation can still take place at unoxidized centers after the film has set. Such oxidative degradation might generally be expected to have an adverse effect upon many of the properties of the dried films.

Linseed oil is thus a good drying vehicle because the average functionality of its molecules approaches 2. The functionality ranges from 3 for a fair proportion down to 1 and even to 0 for a few. The proportions of molecules having the various functionalities of 0, 1, 2, and 3 may be far from ideal, but nevertheless linseed oil conforms much better than the special vehicles to the requirements for the formation of a suitable hard film, at the same time leaving a minimum of vulnerable points in the film for subsequent oxidative attack and degradation.

Present evidence indicates that in linseed oil the proportions of simple triglycerides (that is, triglyceride molecules containing a single fatty acid) are quite small. The fatty acids are distributed in such manner that there are significant amounts of linoleo dilinolenin (approximately trifunctional) and quite large proportions of molecules containing a single saturated or monounsaturated fatty acid together with two polyunsaturated fatty acids (approximately bifunctional).

3. Similar considerations help to explain disappointing correlations between film properties and fatty acid composition of the

Federation compounds. Since oleic acid has but one double bond, drying could not occur by polymerization of conjugated systems. Film formation in the case of SO oleic PE alkyd, the one oleate compound which did dry, probably did not involve the oleic radicals, nor, indeed, any appreciable amount of primary valence linkages other than those already present as PE-phthalate ester bonds.

In eleostearate compounds, conjugated systems were already present and mere traces of oxidation were involved in polymerization reactions. No discernible amounts of hydroperoxide were formed and thus film modifications due to hydroperoxide reactions did not occur.

Drying reactions of linoleates and linolenates did not resemble those of either oleates or eleostearates but were similar to each other; in these two types of compounds the properties of films could best be correlated with structure. But even here, differences in kinetics and in the nature of secondary products were sufficient to interfere with such correlation.

4. On the other hand, within a series of compounds representing a single fatty acid, certain observations of relationships between properties and alcohol functionality could be made. To some extent these properties depended upon increased proportions of oxidizable fatty acids with increasing alcohol functionality. Even with the triglycerides, as noted above, the functionality of 3 (except in the case of oleates) was about 50% more than needed for the formation of hard films.

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CHAPTER XIV

Statistical Analysis of Data

The key purpose of the whole Federation program was to discover new relationships among a number of properties and certain controlled variables in drying and aging films. Such discovery depends chiefly upon the application of intuitive mental processes and inductive reasoning.

Scientists increasingly recognize, however, that another tool, statistical analysis, can greatly assist these methods in making correct interpretations of the data of a research of this sort. The Evaluation Committee therefore tabulated, on forms prepared for the purpose, all the results that could be examined by statistical methods, and turned them over to Dr. E. B. FitzGerald of the Marshall Laboratory of E. I. du Pont de Nemours & Co., Inc. He carried out the monumental task of calculation and comparison, the results of which are presented here.

Objectives

At the outset, it must be pointed out that the program was not based primarily on a statistical design. Although uniform drying conditions, times, etc., were to be observed in so far as possible, the data of some of the projects were entirely unsuited for statistical treatment. Some of the others were not amenable to such treatment because the projects were not specifically designed for it, and their tabulated data yielded only partial advantage. A few of the tables of results used in this study are found in the preceding chapters; the others (Tables XIV-1 to XIV-38) are on pages 352 to 380, and the general summary of the statistical analysis is in Table XIV-39 on pages 382 to 385.

There are three general types of limitations on the value of the data of this program, when seeking statistical relationships.

1. Insufficiently wide coverage of data. Example: Because glycerol, pentaerythritol, and dipentaerythritol are the alcohols of most practical interest to paint formulators, only these three were employed in making the standard compounds for the program.

TABLE XIV-1

Project 1, Gain in Weight, Scofield Data: Time to Set, Hours

Type vehicle	Fatty acid component Oleic*	Linoleic	Linolenic	Eleo-stearic
Glyceryl ester		9.2	5.2	
PE ester	Indef.	5.2	2.5	
DiPE ester	Indef.	4.4	1.9	
LO glycerol alkyd		2.2	1.0	1.9
SO glycerol alkyd		3.5	1.4	
LO PE alkyd	Indef.	2.7	1.5	
SO PE alkyd	Indef.			

Varnish linseed oil	Commercial alkyd*
4.7	3.3

* Oleic esters showed a very slight loss in weight with no end point. Rate and amount of gain for eleostearic esters are doubtful. Nonvolatile content of commercial alkyd could not be precisely determined.

TABLE XIV-2

Project 1, Gain in Weight, Scofield Data: Amount and Rate of Gain to Setting Time, as Per Cent of Nonvolatile Sample Weight

Type vehicle	Fatty acid component Oleic*		Linoleic		Linolenic	
	Amt.	Rate	Amt.	Rate	Amt.	Rate
Glyceryl ester			12.7	1.3	17.8	3.4
PE ester	None		11.3	2.2	14.9	6.0
DiPE ester	None		12.8	2.9	13.3	6.9
LO glycerol alkyd			5.2	2.4	4.3	4.3
SO glycerol alkyd			3.5	1.0	2.1	1.5
LO PE alkyd	None		5.1	1.9	6.7	4.5
SO PE Alkyd	None					

Varnish linseed oil		Commercial alkyd*	
Amt.	Rate	Amt.	Rate
13.7	2.9	—	—

* See footnote to Table XIV-1.

TABLE XIV-3
Project 1, Gain in Weight, Williams Data: Specific Gravity of Films

	Fatty acid component							
	Oleic		Linoleic		Linolenic		Eleostearic	
Type vehicle	With drier	Without drier	With drier	Without drier	With drier	Without drier	With drier	Without drier
Glyceryl ester								
1 week*			0.9101	0.9769	0.9689	1.0840	0.8379	0.7830
1 month			1.0796	0.9850	1.1099	1.1011	1.0429	1.1780
3 months			1.0995	1.0668	1.0485	1.0345	1.1797	1.1759
PE ester								
1 week	†	†	1.0605	1.0155	1.0823	1.0541	1.0904	1.0866
1 month	†	†	1.0544	1.0742	—	1.0694	1.0632	1.0194
3 months	†	†	1.0592	1.0673	1.1363	1.1244	1.0828	1.0840
DiPE ester								
1 week	†	†	1.0593	1.0213	1.0278	1.1108		
1 month	†	†	1.0441	0.9899	1.1114	1.1581		
3 months	†	†	1.1086	1.1181	1.1615	1.1881		
LO glycerol alkyd								
1 week			1.0805	0.9303	1.1520	1.1299	1.1410	1.0794
1 month			1.1723	1.0771	1.0932	1.1591	1.1781	1.1012
3 months			1.1211	1.1811	1.2094	1.1970	1.0900	1.1368
SO glycerol alkyd								
1 week			1.0844	1.1745	†	1.1317‡		
1 month			1.2115	1.1708	1.3088	1.1702		
3 months			1.1415	1.1827	1.2177	1.2310		
LO PE alkyd								
1 week	†	†	1.0456	1.0817	1.0637	1.1131		
1 month	†	†	1.1323	1.1137	1.1282	1.1851		
3 months	†	†	1.1584	1.1114	1.1396	1.1568		
SO PE alkyd								
1 week	§	§						
1 month	1.1853	§						
3 months	§	§						

	Varnish linseed oil		Dehydrated castor oil		Commercial alkyd	
	With drier	Without drier	With drier	Without drier	With drier	Without drier
1 week	0.9944‡	0.9700	1.0221	†	1.0800	†
1 month	0.9213‡	0.9702	1.0200	†	1.1638	1.1051
3 months	1.0707	1.0546	1.0310	†	1.1423	1.1010

* Values taken with water.
† Film not dry.
‡ Film dry at top, tacky at bottom.
§ Film flaked when scraped.

Hence, from a statistical point of view there is some uncertainty in the relationship between the properties of an ester and the functionality of the alcohol it contains. It would be desirable, from this standpoint, to establish a special research project involving esters of a more complete series of alcohols.

2. Omissions of data due to experimental difficulties. Examples:

TABLE XIV-4

Project 2, Ultimate Analysis: Atoms of Oxygen per Mole of Compound

	Fatty acid component			
Type vehicle	Oleic	Linoleic	Linolenic	Eleostearic
Glyceryl ester				
1 week		18.2	22.0	20.2
30 days		19.2	23.5	20.8
365 days		20.7	23.5	24
PE ester				
1 week		22.0	20.3	22.5
30 days		22.0	23.7	27.3
365 days		29.5	24.5	27.5
DiPE ester				
1 week		33.0	36.0	
30 days		35.0	38.0	
365 days		39.0	41.5	
LO glycerol alkyd				
1 week		16.0	13.0	14.0
30 days		16.5	14.0	14.5
365 days		27.2	25.3	24
SO glycerol alkyd				
1 week		14.5	10.9	11.6
30 days		14.9	11.5	12
365 days		25.5	23.8	24.1
LO PE alkyd				
1 week		21.1	18.3	
30 days		21.5	19.2	
365 days		22.0	20.7	
SO PE alkyd				
1 week	16.7			
30 days	18.5			
365 days	20.5			

In many of the projects, oleate esters could not be tested because they failed to dry. Some of the eleostearate compounds gelled before the experiments could be started, or their films wrinkled so badly that no data (or at least none of statistical value) could be obtained.

3. No estimate of error. Example: Variations in experimental factors made it impracticable or impossible in many cases, even where averages of several measurements were obtained, to estimate standard deviations and confidence limits. In many other cases replicate determinations of the same datum were not feasible or possible, and thus calculations of error could not be made.

Under these circumstances the role of statistics must be confined

TABLE XIV-5

Project 3, Solvent Resistance: Per Cent Insoluble in Carbon Tetrachloride

Type vehicle	Oleic	Fatty acid component Linoleic	Linolenic	Eleostearic
Glyceryl ester				
7 days		54.0	67.5	60.0
30 days		62.0	75.0	63.0
365 days		81.0	75.0	66.5*
PE ester				
7 days		70.0	92.5	67.5
30 days		81.0	95.0	72.0
365 days		86*	95.5	79.5
DiPE ester				
7 days		78.0	95.0	
30 days		78.5	95.5	
365 days		78.5	95.5	
LO glycerol alkyd				
7 days		76.0	84.0	82.0
30 days		82.0	87.0	84.0
365 days		92.0*	93*	88*
SO glycerol alkyd				
7 days		84.5	80.5	75.0
30 days		84.5	85.5	81.5
365 days		84.5*	89.5*	92.5*
LO PE alkyd				
7 days		71.0	82.5	
30 days		74.5	88.0	
365 days		80	90.5	
SO PE alkyd				
7 days	83.0			
30 days	91.5			
365 days	92.5*			

	Varnish linseed oil	Dehydrated castor oil	Commercial alkyd
7 days	48.0	60.5	72.0
30 days	61.0	67.0	74.0
365 days	84.5*	76*	78*

* Extrapolated values.

to detection of broad, general relationships having a high degree of certainty. At the same time it can serve the auxiliary function of pointing out weaknesses in the data in a way that will benefit the

TABLE XIV-6
Project 4, Stress-Strain Measurements: Rate of Change in Distensibility
(*d* log distensibility/*d* log time)

Type vehicle	Fatty acid component Linoleic	Linolenic	Eleostearic
Glyceryl ester	—	−1.26	−0.92
PE ester	—	−1.12	−0.64
LO glycerol alkyd	−0.83	−0.83	
SO glycerol alkyd	−0.83	−0.83	

Varnish linseed oil	Commercial alkyd
−2.44	−0.57

The above values represent the rates in the interval 2–32 weeks; the logarithmic plots were linear within this region. Clear and pigmented materials yielded identical values.

TABLE XIV-7
Project 8, Outdoor Weathering: Months to Start of Peeling for Clear and Pigmented Films

	Fatty acid component							
	Oleic		Linoleic		Linolenic		Eleostearic	
Type vehicle	Clear	Pigmented	Clear	Pigmented	Clear	Pigmented	Clear	Pigmented
Glyceryl ester			20+	20+	13	4	20+	10
PE ester		18+	20+	20+	18	2.5	20+	13
DiPE ester		18+		20+	19	3		
LO glycerol alkyd			9	10	7	7−	7	10
SO glycerol alkyd			7	8	7	3		
LO PE alkyd	19	20+	19	10	7	4		
SO PE alkyd	7	8						

Varnish linseed oil		Dehydrated castor oil		Commercial alkyd	
Clear	Pigmented	Clear	Pigmented	Clear	Pigmented
20+	20+	20+	20+	20	13

Leaded outside white paint	Lead-free outside white paint	Commercial enamel
20+	20+	20+

design of additional experiments based on the results of this program, and also exclude unwarranted conclusions from the present work.

Methods

Since the data for linoleic and linolenic esters and alkyds were complete in nearly all the tables, this portion of every table was

TABLE XIV-8

Project 8, Outdoor Weathering: Peeling Rating of Films at 20 Months

	Fatty acid component							
	Oleic		Linoleic		Linolenic		Eleostearic	
Type vehicle	Clear	Pig- mented	Clear	Pig- mented	Clear	Pig- mented	Clear	Pig- mented
Glyceryl ester			10	10	4	2*	10	2*
PE ester		10†	10	10	8	1	10	8*
DiPE ester		10†	—	10	8	1		
LO glycerol alkyd			2	2	0	1	0	8
SO glycerol alkyd			0	0	0	1		
LO PE alkyd	8	10	9	6*	0	1		
SO PE alkyd	0	0						

Varnish linseed oil		Dehydrated castor oil		Commercial alkyd	
Clear	Pigmented	Clear	Pigmented	Clear	Pigmented
10	10	10	10	9	9

Leaded outside white paint	Lead-free outside white paint	Commercial enamel
10	10	10

* Bad scaling also.
† Exposed 18 months.

TABLE XIV-9

Project 8, Outdoor Weathering: Loss of Gloss of Pigmented Films

Column *A:* Number of weeks for loss of 50% of original gloss.
Column *B:* Number of weeks for Glossmeter reading to fall to 10–11 per mil.

	Fatty acid component							
	Oleic		Linoleic		Linolenic		Eleostearic	
Type vehicle	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Glyceryl ester			16	5	3	6	4	9
PE ester	7	9	2−	5	5	6	6	9
DiPE ester	5	8	4	5	4	6		
LO glycerol alkyd			13	16	8	13	10	13
SO glycerol alkyd			6	13	7	13		
LO PE alkyd	4	10	9	13	7	10		
SO PE alkyd	6	9						

Varnish linseed oil		Dehydrated castor oil		Commercial alkyd	
A	*B*	*A*	*B*	*A*	*B*
5	14	8	13	5	13

Leaded outside white paint		Lead-free outside white paint		Commercial enamel	
A	*B*	*A*	*B*	*A*	*B*
5	10	7	12	24+	24+

TABLE XIV-10

Project 8, Outdoor Weathering: Development of Chalking for Pigmented Films

Column *A:* Number of weeks to first chalking.

Column *B:* Number of weeks for chalk rating to fall to 6.

Column *C:* Number of weeks for chalk rating to fall to 2.

	Fatty acid component											
	Oleic			Linoleic			Linolenic			Eleostearic		
Type vehicle	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
Glyceryl ester				4	6	8	5	6	7	7	8	9
PE ester	6	6–7	8	5	7	9	5	6–7	8	9	8	9
DiPE ester	6	6–7	8	5	7	8	5	6	8			
LO glycerol alkyd				18	18	18—*	9	11	13–14	11	13–14	18
SO glycerol alkyd				9	9	11	9	8	12—			
LO PE alkyd	9	9	12	12	11	15—	9	8	11			
SO PE alkyd	6	7	9									

Varnish linseed oil			Dehydrated castor oil			Commercial alkyd		
A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
5	8	9	11	12	15	8	9	15

Leaded outside white paint			Lead-free outside white paint			Commercial enamel		
A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
11	13	18	11	18	20—	†	†	†

* Chalk rating of 1 after 20 months.

† Chalk rating of 10 at 18 weeks, falling to 2 (without intermediate readings) at 20 months.

tested for three main effects. These can best be described by reference to the following representation of a typical table:

	Linoleic	Linolenic
Glyceryl ester	a	b
PE ester	c	d
DiPE ester	e	f
LO glycerol alkyd	g	h
SO glycerol alkyd	i	j
LO PE alkyd	k	l

where a, b, c, etc., are the numerical values of some property.

1. *Acid effect.* If the relation $a<b$, $c<d$, $e<f$ was found to hold

TABLE XIV-11

Project 9, Water and Alkali Tests: Water Immersion of Clear Films

Column *A:* Ratings of 1950 water tests.
Column *B:* Ratings of 1951 water tests.
Column *C:* Combined ratings, 1950 and 1951.

	Fatty acid component											
	Oleic			Linoleic			Linolenic			Eleostearic		
Type vehicle	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
Glyceryl ester				2	3	2.5	6	5	5.5	4	3	3.5
PE ester				4	4	4	4	—	4	4	3	3.5
DiPE ester				4	5	4.5	4	—	4			
LO glycerol alkyd				10	7	8.5	10	10	10	10	8	9
SO glycerol alkyd				10	8	9	4	8	6			
LO PE alkyd	—	(4)*	4	4	3	3.5	6	—	6			
SO PE alkyd	6	6	6									

Varnish linseed oil			Dehydrated castor oil			Commercial alkyd		
A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
3	—	3	4	—	4	6	—	6

* Based on performance at 30- and 90-day drying periods only; film not dry at 7 days.

TABLE XIV-12

Project 9, Water and Alkali Tests: Alkali Immersion of Clear Films

Column *A:* Ratings of 1950 alkali tests.
Column *B:* Ratings of 1951 alkali tests.
Column *C:* Combined ratings, 1950 and 1951.

	Fatty acid component											
	Oleic			Linoleic			Linolenic			Eleostearic		
Type vehicle	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
Glyceryl ester				2	2	2	2	4	3	1	4	2.5
PE ester				2	4	3	2	—	2	1	4	2.5
DiPE ester				6	4	5	2	—	2			
LO glycerol alkyd				6	8	7	6	9	7.5	8	7	7.5
SO glycerol alkyd				6	7	6.5	6	9	7.5			
LO PE alkyd	—	(4)*	4	5	6	5.5	4	—	4			
SO PE alkyd	6	6	6									

Varnish linseed oil			Dehydrated castor oil			Commercial alkyd		
A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
1	—	1	3	—	3	9	—	9

* Based on performance at 30- and 90-day drying periods only; film not dry at 7 days.

TABLE XIV-13

Project 9, Water and Alkali Tests: Overall Ratings, Both Tests, Both Years

	Fatty acid component			
Type vehicle	Oleic	Linoleic	Linolenic	Eleostearic
Glyceryl ester		2+	4+	3
PE ester		3.5	3	3
DiPE ester		5−	3	
LO glycerol alkyd		8−	9−	8+
SO glycerol alkyd		8−	7−	
LO PE alkyd	4	4.5	5	
SO PE alkyd	6			

Varnish linseed oil	Dehydrated castor oil	Commercial alkyd
2	3.5	7.5

by a statistically significant margin at the 95% confidence level, the acid effect for esters was recorded as positive. This means that it is 95% certain that the value of the given property is higher for a linolenic acid ester than for a linoleic ester of the same alcohol. If the opposite effect, i.e., $a>b$, etc., was found to prevail, the acid effect was called negative. These designations are used in Table XIV-39 at the end of this chapter, which summarizes all the findings.

The simple existence of the relation $a<b$, $c<d$, $e<f$ is by no means a sufficient condition to define a positive acid effect; the differences a — b, etc., as well as the absolute level of values concerned, are taken into account by the calculation. Details of the method are explained by Youden (2) and in many other texts on statistics.

Similar remarks apply to the acid effect for alkyds. In some cases, where no acid effect was found for either alkyds or esters by themselves, corresponding values from the two parts of the table were combined according to suitable procedures and tested for "combined acid effect." The improved precision resulting from this treatment yielded occasional good results.

2. Alcohol effect. In applying the same standards and similar means, in some instances the relationship $a<c<e$ and $b<d<f$ was found to be statistically significant. This means that the measured property increases in the same direction as alcohol functionality for both linoleic and linolenic esters. It does not imply that the property

TABLE XIV-14

Project 10, Yellowing of Pigmented Compounds (Data in Trichromatic Coefficient Units)

Column *A:* Net yellowing in first 50 days.
Column *B:* Average yellowness between 50 and 385 days.

Type vehicle	Fatty acid component							
	Oleic		Linoleic		Linolenic		Eleostearic	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Glyceryl ester								
In light			.0030	.0113	.0073	.0228	.0047	.0167
In dark			.0188	.0275	.0290	.0528	.0295	.0467
PE ester								
In light	*	.0072	.0040	.0112	.0104	.0267	.0060	.0176
In dark	*	.0103	.0162	.0265	.0354	.0544	.0265	.0417
DiPE ester								
In light	*	.0078	.0043	.0125	—	—		
In dark	*	.0082	.0160	.0268	—	—		
LO glycerol alkyd								
In light			.0070	.0141	.0129	.0211	.0103	.0217
In dark			.0094	.0185	.0203	.0327	.0105	.0233
SO glycerol alkyd								
In light			.0065	.0127	.0114	.0206		
In dark			.0074	.0157	.0171	.0300		
LO PE alkyd								
In light	*	.0066	.0086	.0134	.0139	.0234		
In dark	*	.0073	.0153	.0244	.0211	.0393		
SO PE alkyd								
In light	.0049	.0099						
In dark	.0028	.0098						

	Varnish linseed oil		Dehydrated castor oil		Commercial alkyd	
	A	*B*	*A*	*B*	*A*	*B*
In light	.0034	.0152	.0037	.0104	.0058	.0123
In dark	.0170	.0318	.0066	.0157	.0072	.0157

* Not dry in 50 days.

is proportional to functionality, and in order to avoid such an implication, the relationship is hereafter referred to simply as a direct or positive alcohol effect. The reverse order $a>c>e$ and $b>d>f$ is called an inverse relationship to functionality or a negative alcohol effect.

TABLE XIV-15

Project 13, Erosion: Chalking of Pigmented Compounds

	Fatty acid component			
Type vehicle	Oleic	Linoleic	Linolenic	Eleostearic
Glyceryl ester		2	2	2
PE ester	0	2	8	2
DiPE ester	0	2	8	
LO glycerol alkyd		8	10	6
SO glycerol alkyd		10	8	0
LO PE alkyd	0	8	10	
SO PE alkyd	10			

Varnish linseed oil	Dehydrated castor oil	Commercial alkyd
2	8	10

Key; 10 none, 8 very slight, 6 slight, 4 medium, 2 heavy, 0 not measurable.

TABLE XIV-16

Project 13, Erosion: Accelerated Weathering, Weeks to Failure

	Fatty acid component							
	Oleic		Linoleic		Linolenic		Eleostearic	
Type vehicle	Clear	Pigmented	Clear	Pigmented	Clear	Pigmented	Clear	Pigmented
Glyceryl ester			*	12	26	10	—	9
PE ester	*	—	23	11	11	9	23	12
DiPE ester	*	—	12	16	20	9		
LO glycerol alkyd			18	25	17	18	11	26
SO glycerol alkyd			31	29	13	12		
LO PE alkyd	25	—	14	15	7	6		
SO PE alkyd	32	6						

Varnish linseed oil		Dehydrated castor oil		Commercial alkyd	
Clear	Pigmented	Clear	Pigmented	Clear	Pigmented
*	14	30	29	31	44

* Did not dry within reasonable time.

For the alkyds, a positive alcohol effect was taken to mean that the numerical value of a measured property was significantly greater for the PE alkyds than for either of the glycerol types, regardless of

TABLE XIV-17

Project 13, Erosion: Gloss Retention in Weather-Ometer

Column *A:* Sum of gloss readings on clear vehicles after 6, 12, 18, and 24 periods of 115 hours each.

Column *B:* Sum of gloss readings on pigmented compounds after 6, 12, 18, 24. 30, and 36 periods of 115 hours each.

Column *C:* Combined rating on a scale of 10 for both clear and pigmented compounds.

Type vehicle	Fatty acid component											
	Oleic			Linoleic			Linolenic			Eleostearic		
	A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
Glyceryl ester				0	1	0	115	1	2.5	0	1	0
PE ester	0	0	0	97	2	2	59	3	2	53	1	1
DiPE ester	0	0	0	90	1	2	96	2	2			
LO glycerol alkyd				147	79	8	50	35	3.5	81	13	2.5
SO glycerol alkyd				232	110	10	135	52	6	0	0	0
LO PE alkyd	139	0	3	129	17	4	0	30	2			
SO PE alkyd	290	14	7									

Varnish linseed oil			Dehydrated castor oil			Commercial alkyd		
A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
0	3	0	106	18	3.5	203	68	9

acid modification. That is: $g<k>i$ and $h<l>j$ represents the positive, and $g>k<i$ and $h>l<j$ the negative, effect.

3. Oil effect. In many cases the measured values of a property fell into the pattern: oil esters>long-oil alkyds>short-oil alkyds, regardless of the particular acids or alcohols involved. This relationship is hereafter referred to as direct or positive; its inverse occurs frequently as well. Suitable tests were devised to detect the oil effect and determine its significance; these tests were applied to nearly every table of data except those in which the measured property was referred to unit oil (or fatty acid) content.

In addition to the three main effects, some of the projects contained data which brought out additional relationships amenable to calculation: pigmented vs. clear, light exposure vs. dark, behavior of oleic and eleostearic compounds, etc. The discussion which follows describes these, where they occur.

Finally, it must be reiterated that where estimates of error are lacking for each experimental datum, the statistical method is

TABLE XIV-18

Project 13, Erosion: Weight Loss in Weather-Ometer

Column *A:* Clear vehicles, losses in milligrams.

Column *B:* Pigmented compounds, losses in milligrams.

Column *C:* Combined rating on weight losses for clear and pigmented compounds.

	Fatty acid component											
	Oleic			Linoleic			Linolenic			Eleostearic		
Type vehicle	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
Glyceryl ester												
After 6 hours				—	80		118	72		—	54	
After 12 hours				—	122	2	136	108	4.5	—	74	3.5
PE ester												
After 6 hours	—	17		108	48		86	48		124	56	
After 12 hours	—	34	5	122	76	5	160	112	4	158	78	4
DiPE ester												
After 6 hours	—	—		114	62		80	46				
After 12 hours	—	—	0	152	120	3.5	118	62	6			
LO glycerol alkyd												
After 6 hours				36	20		18	4		48	36	
After 12 hours				58	38	8.5	58	8	10	168	58	6
SO glycerol alkyd												
After 6 hours				10	16		28	10				
After 12 hours				14	42	10	70	34	9			
LO PE alkyd												
After 6 hours	46	—		28	36		42	—				
After 12 hours	53	—	2.5	32	85	8	128	—	2.5			
SO PE alkyd												
After 6 hours	29	22										
After 12 hours	34	46	9									

	Varnish linseed oil			Dehydrated castor oil			Commercial alkyd		
	A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
After 6 hours	—	80		118	58		36	28	
After 12 hours	—	28	4	150	68	4.5	40	38	9

powerless to separate error from interaction. That is, the deviation of a single entry in a table from an otherwise apparent trend followed by all the others may be due to error in the measurement, or it may be that the deviation is a valid effect caused by some unknown behavioral relationship of a particular material to a particular

TABLE XIV-19

Project 13, Erosion: Rating of Clear and Pigmented Films on Appearance

Type vehicle	Fatty acid component Oleic	Linoleic	Linolenic	Eleo-stearic
Glyceryl ester		5	5	2
PE ester	0	5.5	5.5	5
DiPE ester	0	3.5	6.5	
LO glycerol alkyd		7.5	6	6
SO glycerol alkyd		10	5.5	0
LO PE alkyd	3	6	5.5	
SO PE alkyd	8.5			

Varnish linseed oil	Dehydrated castor, oil	Commercial alkyd
2.5	9	10

test. Such special relationships cannot be detected statistically and they are not further considered.

Discussion

Project 1, Gain in Weight

Table XIV-1 indicates that linolenic esters and alkyds set faster than corresponding linoleic compounds. If it is supposed that the setting process is related to gain in weight, the table might lead one to infer that linolenic compounds either gain weight faster or set at smaller gain (or do both simultaneously) than linoleic. Table XIV-2, which gives rate of gain, substantiates the first assumption. No conclusion can be drawn as to the amount of gain at the set point, for this table contains too much error and/or interaction; but it is clear that both rate and total amount of gain at set are greater for simple esters than for alkyds. This is consistent with the idea that the setting process in part involves reaction at or near unsaturated centers of the fatty acids, since there are more of these in the oils than in the alkyds. It is also consistent with the fact that polymeric materials can set with less reaction (i.e., cross-linking) than monomers.

Excessive error and interaction in Tables IV-30 and IV-31 (page 73) preclude any inferences regarding the amount or the time of

TABLE XIV-20

Project 22, Hardness and Abrasion Resistance: Sward Rocker Hardness

Column *A:* Sward rocker hardness of clear films.

Column *B:* Sward rocker hardness of pigmented films.

Column *C:* Combined hardness ratings on clear and pigmented films at both ages.

	Fatty acid component											
Type vehicle	Oleic			Linoleic			Linolenic			Eleostearic		
	A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
Glyceryl ester												
After 8 days				0	6		4	5.5		*	4	
After 3 months				1	6	1.5	6	6	2	*	6	1
PE ester												
After 8 days	*	*		0	6		5	6		0	4	
After 3 months	*	*	0	3	8	1.5	5	10	2.5	2	8	1.5
DiPE ester												
After 8 days	*	*		—	5		—	6				
After 3 months	*	*	0	—	6	1	—	10	1.5			
LO glycerol ester												
After 8 days				24	8		20	3		27	3	
After 3 months				28	32	9	24	26	7.5	30	6	6.5
SO glycerol alkyd												
After 8 days				11	13		4	4				
After 3 months				20	26	7	23	42	7.5			0
LO PE alkyd												
After 8 days	*	*		12	10		30	18				
After 3 months	*	*	0	15	16	5.5	30	28	10			
SO PE alkyd												
After 8 days	21	13										
After 3 months	25	16	7.5									

	Varnish linseed oil			Dehydrated castor oil			Commercial alkyd		
	A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
After 8 days	0	6		0	9		10	7	
After 3 months	0	8	1.5	0	10	2	11	12	4

* Film not dry enough to test.

maximum gain in the presence of drier, but in the absence of drier linolenic esters not only reach a higher maximum than corresponding linoleates but they do so in less time. That the tables do not yield similar conclusions for alkyds is probably due to the lower value of their maxima, with consequent masking of the effects by error and

TABLE XIV-21

Project 22, Hardness and Abrasion Resistance: Abrasion Coefficients and Ratings

Column *A:* Abrasion coefficient in liters per mil for clear films.

Column *B:* Abrasion coefficient in liters per mil for pigmented films.

Column *C:* Combined ratings for clear and pigmented films.

	Fatty acid component											
	Oleic			Linoleic			Linolenic			Eleostearic		
Type vehicle	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
Glyceryl ester				1	11.7	2.5	1	14.2	5	*	9.4	2
PE ester	*	*	0	18.9	9.7	6	31.5	12.6	9	†	11.7	
DiPE ester	*	*	0	—	11.2	2	—	8.9	2			
LO glycerol alkyd				9.8	11.2	4	19.2	—	4	14.9	10.6	5.5
SO glycerol alkyd				13.2	7.9	4	17.6	4.2	6.5			0
LO PE alkyd	*	*	0	10.2	8.4	3.5	23.4	27–	10			
SO PE alkyd	5.4	4.1	2									

Varnish linseed oil			Dehydrated castor oil			Commercial alkyd		
A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
*	9.5	2	*	18.0	3.5	11.7	7.5	4

* Film not dry enough for test.

† Film too irregular for test.

TABLE XIV-22

Projects 13 and 22, Erosion, Hardness, and Abrasion Resistance: Total Rating for Both Clear and Pigmented Films

	Fatty acid component			
Type vehicle	Oleic	Linoleic	Linolenic	Eleostearic
Glyceryl ester		2.2	3.8	1.7
PE ester	1.0	4.0	4.6	2.9
DiPE ester	0.0	2.4	3.6	
LO glycerol alkyd		7.4	6.2	5.3
SO glycerol alkyd		8.2	6.9	0.0
LO PE alkyd	3.0	5.4	6.0	
SO PE alkyd	6.8			

Varnish linseed oil	Dehydrated castor oil	Commercial alkyd
2.0	4.5	7.2

TABLE XIV-23

Projects 14 and 19, Porosity and Permeability: Permeability of Films to Water Vapor

Column *A:* Average permeability constant × 10^7 for clear unsupported films.
Column *B:* Number of samples measured.
Column *C:* Average film thickness in mils.

Type vehicle	Fatty acid component											
	Oleic			Linoleic			Linolenic			Eleostearic		
	A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
Glyceryl ester				9.4	1	1.09	0.99	2	1.92	1.12	2	0.28
PE ester	—			2.14	3	1.08	0.60	2	1.38	0.52	4	0.27
DiPE ester	16.0	1	2.96	2.69	6	1.15	0.75	3	1.36			
LO glycerol alkyd				1.75	7	1.06	0.97	5	1.09	0.96	7	0.99
SO glycerol alkyd				1.22	7	1.26	0.82	3	0.77			
LO PE alkyd	5.26	7	0.89	0.89	8	0.72	0.94	7	0.87			
SO PE alkyd	1.46	4	1.14									

Varnish linseed oil			Dehydrated castor oil			Commercial alkyd		
A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
9.2	2	1.62	6.2	4	1.67	1.05	17	0.62
5.43	9	0.53	2.12	6	0.83			

interaction. Combining the data for all compounds in these two tables reveals, interestingly, that maximum gain in weight is greater in the absence of drier than in its presence.

Table XIV-3 brings out only one relationship between specific gravity and structure: alkyds are more dense than corresponding pure esters. Density increases with time for almost all materials and this relationship is not influenced except ratewise, by the presence of driers.

Set-to-touch time with drier (Table IV-32, page 74) shows no recognizable correlation with structure at the usual 95% confidence level. However, on dropping to the 90% level, set-to-touch time is found to decrease in the order linoleic, linolenic, eleostearic for the oils. Whereas ordinarily a 90% level is not acceptable, it appears justified in this case, since the setting time without drier is probably

TABLE XIV-24

Projects 14 and 19, Porosity and Permeability: Permeability of Alkyd Films to Liquid Water

Column *A:* Liquid water permeability constant × 10^7 for clear unsupported films.

Column *B:* Water vapor permeability constant × 10^7, measured on the same films.

Column *C:* Film thickness in mils.

	Fatty acid component								
	Linoleic			Linolenic			Eleostearic		
Type vehicle	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
LO glycerol alkyd	0.44	1.47	1.38	0.31	0.90	0.99	0.32	1.23	1.15
SO glycerol alkyd	0.42	1.28	1.04	0.52	1.10	0.97			
LO PE alkyd		0.94	3.09	1.06	0.57	0.48	1.12		

Commercial alkyd		
A	*B*	*C*
0.55	1.65	1.45

TABLE XIV-25

Project 16, Molecular Size, Shape, and Weight: Molecular Cross-Section Areas

Column *A:* Areas (by Langmuir balance) in sq. cm. × 10^{16} at zero film pressure.

Column *B:* Areas in sq. cm. × 10^{16} at crumpling pressure.

	Fatty acid component							
	Oleic		Linoleic		Linolenic		Eleo-stearic	
Type vehicle	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Glyceryl ester			179	127	183	136	136	102
PE ester	228	185	213	174	249	199	200	121
DiPE ester	326	251	293	227	337	299		
LO glycerol alkyd			426	251	443	263	425	234
SO glycerol alkyd			849	388	801	392	811	373
LO PE alkyd	537	357	438	318	610	475		
SO PE alkyd	1845	1090						

a closely related phenomenon and it corroborates this trend. Furthermore, on taking averages, the results are even better. It should be noted that these remarks apply only to oil esters; the data for alkyds

TABLE XIV-26

Project 16, Molecular Size, Shape, and Weight: Crumpling Force Data

Column *A:* Force at crumpling point in dynes per centimeter.

Column *B:* Value of constant x in equation of state for "liquid" two-dimensional systems, $F(A - b) = kTx$

Type vehicle	Fatty acid component							
	Oleic		Linoleic		Linolenic		Eleostearic	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Glyceryl ester			11.3	.345	8.9	.301	19.6	.210
PE ester	11.1	.393	10.2	.170	11.2	.346	18.4	.423
DiPE ester	14.5	.45	11.4	.388	11.1	.270		
LO glycerol alkyd			14.8	.597	12.1	.575	17.9	.691
SO glycerol alkyd			18.6	1.45	16.8	1.94	26.0	1.19
LO PE alkyd	16.8	1.02	14.3	.539	9.2	.513		
SO PE alkyd	20.2	3.02						

in this table permit no conclusions within the acceptable range of confidence.

Table IV-33, page 74, loss in weight on baking with and without drier, shows that linoleic esters lose more weight than linolenic. The data for eleostearic esters are inconclusive, as are those for all alkyds. The table also shows that glyceryl esters lose appreciably more weight than PE or diPE esters; with drier, the trend exists but is not large enough to be statistically reliable. In none of the data in Tables IV-32 and IV-33 is there any satisfactory evidence of an oil effect; no systematic variation in properties appears in the order ester > long-oil alkyd > short-oil alkyd, or the reverse. This is somewhat curious, for since both setting time and weight changes presumably depend in part on unsaturation, materials having a high concentration of double bonds (i.e., oil esters) would be expected to differ from the alkyds. Apparently the effect, if it exists, is too small to be detected.

Project 2, Ultimate Analysis

In one isolated instance (Table XIV-4, 1 month) the statistical analysis supports the conclusion that the dried linolenic esters contain more oxygen per original mole of compound than linoleic. This result is greatly weakened by the lack of corroboration at 1 week and 1 year; it is further weakened, if not vitiated, by the existence of the reverse relationship at all times for the alkyds.

TABLE XIV-27

Project 17, Chemical Analysis of Films: Acid Values after Aging

Column *A:* Clear films, aged under standard conditions (Cabinet "B").

Column *B:* Pigmented films, aged under standard conditions (Cabinet "B").

Type vehicle	Fatty acid component							
	Oleic		Linoleic		Linolenic		Eleostearic	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Glyceryl ester								
At 1 week			19.3	30.2	16.0	27.3	30.0	13.6
At 4 weeks			24.9	26.9	30.0	16.8	40.0	14.2
At 16 weeks			48.9	26.6	28.0	17.9	34.0	13.5
PE ester								
At 1 week	8.5	16.5	83.0	23.2	15.0	12.2	52.0	13.1
At 4 weeks	8.0	15.1	40.0	15.8	20.0	14.3	15.0	12.8
At 16 weeks	46.0	14.1	33.0	17.8	21.5	15.9	24.0	12.6
DiPE ester								
At 1 week	7.7	12.5	17.0	13.5	10.2	12.6		
At 4 weeks	14.5	15.8	24.0	17.1	10.5	10.8		
At 16 weeks	23.0	10.1	27.0	11.5	25.0	14.2		
LO glycerol alkyd								
At 1 week			21.5	10.0	13.0	8.7	11.5	11.0
At 4 weeks			12.5	14.8	20.0	9.8	21.5	12.6
At 16 weeks			19.0	10.0	17.0	7.8	12.5	8.4
SO glycerol alkyd								
At 1 week			8.0	14.9	10.6	8.7		
At 4 weeks			27.0	16.8	5.7	9.7		
At 16 weeks			16.5	9.5	13.5	7.7		
LO PE alkyd								
At 1 week	16.0	14.4	9.5	13.8	13.0	13.2		
At 4 weeks	23.5	21.8	20.5	12.6	13.5	10.9		
At 16 weeks	20.0	18.6	15.8	13.3	11.2	13.3		
SO PE alkyd								
At 1 week	23.5	16.9						
At 4 weeks	23.5	18.1						
At 16 weeks	21.6	12.1						

	Varnish linseed oil		Dehydrated castor oil		Commercial alkyd	
	A	*B*	*A*	*B*	*A*	*B*
At 1 week	20.0	27.3	20.0	22.2	11.6	22.5
At 4 weeks	15.0	19.3	7.0	8.8	15.1	52.6
At 16 weeks	21.0	18.9	28.0	15.7	25.0	20.0

TABLE XIV-28

Project 17, Chemical Analysis of Films: Saponification Values after Aging

Column *A:* Clear films, aged under standard conditions (Cabinet "B").

Column *B:* Pigmented films, similarly aged.

Type vehicle	Fatty acid component							
	Oleic		Linoleic		Linolenic		Eleostearic	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Glyceryl ester								
At 1 week			397	103	292	171	585	173
At 4 weeks			203	137	390	208	435	188
At 16 weeks			336	134	243	167	475	159
PE ester								
At 1 week	349	139	386	93	682	150	514	104
At 4 weeks	255	120	504	132	490	167	454	142
At 16 weeks	257	114	370	155	489	179	425	123
DiPE ester								
At 1 week	226	101	492	59	112	43		
At 4 weeks	260	94	365	118	319	79		
At 16 weeks	381	101	476	148	375	134		
LO glycerol alkyd								
At 1 week			397	205	342	194	374	139
At 4 weeks			377	185	478	168	355	152
At 16 weeks			405	173	396	140	466	150
SO glycerol alkyd								
At 1 week			286	157	200	164		
At 4 weeks			472	184	420	139		
At 16 weeks			431	202	410	165		
LO PE alkyd								
At 1 week	360	263	460	178	340	234		
At 4 weeks	440	170	535	158	395	200		
At 16 weeks	423	202	464	161	404	123		
SO PE alkyd								
At 1 week	285	178						
At 4 weeks	275	160						
At 16 weeks	440	216						

	Varnish linseed oil		Dehydrated castor oil		Commercial alkyd	
	A	*B*	*A*	*B*	*A*	*B*
At 1 week	175	—	412	—	438	134
At 4 weeks	390	74	301	68	256	182
At 16 weeks	459	131	364	146	—	179

Comment; These values are averages of duplicate determinations which in many cases differed by as much as 100% of the lower figure.

TABLE XIV-29

Project 17, Chemical Analysis of Films: Pigments Washed from Aged Films
Column *A:* Milligrams of zinc oxide found in washings at 12 weeks.
Column *B:* Milligrams of titanium dioxide found in washings at 12 weeks.

Type vehicle	Fatty acid component: Oleic		Linoleic		Linolenic		Eleostearic	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Glyceryl ester			*	*	*	*		
PE ester	2.27	0.0	1.51	0.02	3.78	0.23	*	*
DiPE ester	1.77	0.02	1.64	0.02	4.03	0.03		
LO glycerol alkyd			0.88	0.0	0.88	0.0	1.0	0.0
SO glycerol alkyd			0.86	0.0	1.01	0.0		
LO PE alkyd	Trace	0.0	1.28	Trace	1.27	Trace		
SO PE alkyd	1.01	Trace						

Varnish linseed oil		Dehydrated castor oil		Commercial alkyd	
A	*B*	*A*	*B*	*A*	*B*
*	*	1.64	0.02	Trace	0.0

* Film deteriorated too much for determination.

TABLE XIV-30

Project 21, Refractive Index of Clear Films: Maximum Refractive Index Readings

Type vehicle	Fatty acid component: Oleic	Linoleic	Linolenic	Eleo-stearic
Glyceryl ester		1.493	1.486	1.520
PE ester	—	1.487	1.494	1.495
DiPE ester	1.485	1.486	1.489	
LO glycerol alkyd		1.488	1.486	1.478
SO glycerol alkyd		1.481	1.481	
LO PE alkyd	1.490	1.491	1.486	
SO PE alkyd	1.480			

Varnish linseed oil	Dehydrated castor oil	Commercial alkyd
1.490	1.495	1.490

Comments: 1. Time to reach maximum varied from 5 minutes to 24 days. 2. Values could not be reproduced with accuracy for a given interval.

Superior uniformity in this respect in the resin data is somewhat surprising, for the O_2 per mole values are definitely smaller for alkyds than for corresponding esters.

TABLE XIV-31

Project 24, Oxidation Studies: Oxygen Absorption

Column *A:* Initial rate of oxygen absorption (estimated from O_2 uptake/time curves) in millimoles O_2 per mole of fatty acid per minute.

Column *B:* Time required to absorb 1 mole O_2 per mole of fatty acid, in hours.

	Fatty acid component							
	Oleic		Linoleic		Linolenic		Eleo-stearic	
Type vehicle	*A*	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Glyceryl ester			3.3	5.8	6.7	1.4	8.3	5.5
PE ester	0.038	448	4.8	5.8	16.7	1.4	4.2	11.6
DiPE ester	0.028	448	4.4	5.8	10.3	1.5		
LO glycerol alkyd			6.7	10.9	3.3	23.5*	2.6	56.
SO glycerol alkyd			4.2	40.0	3.3	23.5*		
LO PE alkyd	0.054	252	4.4	3.0	4.4	3.6		
SO PE alkyd	†	82						

Varnish linseed oil		Dehydrated castor oil		Commercial alkyd	
A	*B*	*A*	*B*	*A*	*B*
5.6	3.5	2.2	10.2	‡	‡

* Time required to absorb 0.95 mole O_2 per mole of fatty acid (maximum O_2 uptake for these compounds).

† Could not be estimated because of induction period.

‡ Not calculated because of unknown fatty acid content of this alkyd.

For esters, the O_2 per mole values increase with increasing alcohol functionality; for alkyds, a similar trend is shown at 1 week and 1 month but it reverses at 1 year and disappears altogether in the average of all times. Finally, in the average of all materials the value of O_2 per mole increases with time but the data do not justify a calculation of rate.

Project 3, Solvent Resistance

The degree of insolubility in carbon tetrachloride after aging (Table XIV-5) is greater for linolenic esters than for corresponding linoleic compounds, up to one month; after this the effect levels out. It increases also with increasing alcohol functionality, but here, too, the effect levels out after the same period. No relationship appears between solubility and oil content. In comparing this last finding

TABLE XIV-32

Project 24, Oxidation Studies: Time (in Hours) for Film to Set*

Type vehicle	Fatty acid component Oleic	Linoleic	Linolenic	Eleo-stearic
Glyceryl ester		7.8	2.5	†
PE ester	984+	5.0	1.0	†
DiPE ester	1800+	3.0	0.9	
LO glycerol alkyd		1.2	1.0	†
SO glycerol alkyd		5.2	5.4	
LO PE alkyd	395	4.8	29.2	
SO PE alkyd	‡			

Varnish linseed oil	Dehydrated castor oil	Commercial alkyd
§	†	0.8

* The "set point" observations were rough approximations, as the samples were not under constant observation. When samples were removed from the Warburg bath, the films were probed with a small glass tube; film was called "set" if it was easily scratched but not tacky and no material adhered to the probe; "hard" if it was difficult to scratch and would chip if more force was used.

† The eleostearates and castor oil were "hard" when the first film examination was made.

‡ "Set" point was not observed; this alkyd was "hard" at 75 hours.

§ "Set" point was not observed; the oil was "hard" at 5 hours.

TABLE XIV-33

Project 24, Oxidation Studies: Oxygen Absorbed at Set Point

Column *A:* Oxygen absorbed at set-to-touch point, mole per mole of fatty acid.

Column *B:* Same, mole per mole of vehicle.

Type vehicle	Fatty acid component Oleic		Linoleic		Linolenic		Eleo-stearic	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Glyceryl ester			1.18	3.54	1.45	4.35	—	—
PE ester	—	—	0.91	3.64	0.88	3.53	—	—
DiPE ester	—	—	0.64	3.84	0.62	3.70		
LO glycerol alkyd			0.14	—	0.25	—	—	—
SO glycerol alkyd			0.65	—	0.68	—	—	—
LO PE alkyd	1.37	—	1.19	—	1.58	—		
SO PE alkyd	—	—						

with those observed in Projects 1 and 2, it must follow that high values of weight gain and O_2 per mole do not necessarily imply decreased solubility.

TABLE XIV-34

Project 24, Oxidation Studies: Maximum Peroxide Content

Column *A:* Time required to reach maximum peroxide content, in hours.

Column *B:* Maximum peroxide content attained, in moles per mole of fatty acid.

Type vehicle	Fatty acid component Oleic		Linoleic		Linolenic		Eleostearic	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Glyceryl ester			8.4	0.53	2.5*	0.58	15.4	0.37
PE ester	405	0.28	7.2	0.47	5.0	0.61	16.0†	0.34
DiPE ester	275	0.27	7.0	0.52	4.2	0.50		
LO glycerol alkyd			5.5	0.47	6.6	0.33	73	0.30
SO glycerol alkyd			8.5	0.38	4.4	0.29		
LO PE alkyd	180	0.20	4.8	0.65	7.7	0.65		
SO PE alkyd	73	0.59						

Varnish linseed oil		Dehydrated castor oil		Commercial alkyd	
A	*B*	*A*	*B*	*A*	*B*
7.3	0.46	17.7	0.37	12	‡

* P.V. showed a maximum after approximately 2.5 hours, then decreased and rose again later to higher values at end of experiment (10.4 hours).

† P.V. showed a maximum after 16 hours, then decreased and rose again to higher values at end of experiment (51.8 hours).

‡ Maximum peroxide value was 1160 meq. per kilogram of unoxidized material.

Project 4, Distensibility

There are so many omissions in the tabulated data (Table XIV-6) that detection of trends and reliability is most difficult. It appears fairly safe to conclude that the rate of decrease in distensibility is directly related to oil content, or in other words, the esters embrittle faster than corresponding alkyds. Even this statement, however, is a little below the 95% confidence level.

Project 8, Outdoor Weathering

Tables XIV-7, XIV-8, XIV-9, and XIV-10 show no statistically significant correlation between properties and structure. A straightforward analysis of the data in Table XIV-9 would lead to the conclusion that linoleic esters lose gloss to a rating of 10 to 11 one week sooner than corresponding linolenic oils. The perfect correlation

TABLE XIV-35

Project 24, Oxidation Studies: Peroxide Content and Disappearance

Column *A:* Peroxide content (mole per mole of fatty acid) when 1 mole O_2 per mole of fatty acid had been absorbed.

Column *B:* Peroxide disappeared at set point (O_2 absorbed − observed P.V.), mole per mole of fatty acid.

Column *C:* Ratio of peroxide value to oxygen absorbed at set point.

	Fatty acid component											
Type vehicle	Oleic			Linoleic			Linolenic			Eleostearic		
	A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
Glyceryl ester				0.50	0.645	0.45	0.50	0.908	0.37	0.28	—	†
PE ester	0.25	—	†	0.41	0.458	0.50	0.50	0.387	0.56	0.28	—	†
DiPE ester	0.17	—	†	0.52	0.146	0.77	0.48	0.192	0.69			
LO glycerol alkyd				0.44	0.000	1.00	0.27*	0.076	0.76	0.31	—	†
SO glycerol alkyd				0.37	0.283	0.56	0.19	0.390	0.43			
LO PE alkyd	0.18	1.25	0.09	0.55	0.615	0.48	0.60	1.098	0.31			
SO PE alkyd	0.58	—	†									

Varnish linseed oil		Dehydrated castor oil		Commercial alkyd	
A, 0.42	*B*, —	*A*, 0.35	*B*, —	*A*, ‡	*B*, —

* At O_2 absorption = 0.95 mole O_2 per mole of fatty acid.

† Set point not observed.

‡ Not calculated because of unknown fatty acid content of this alkyd.

in this respect is probably fortuitous, however, since the data on time to lose 50% of gloss lack significance. For example, if any one of the entries in either of the columns headed "linoleic" or "linolenic" were to be changed by one unit (e.g., 5 changed to 6) the correlation would vanish entirely. The data for alkyds contained nothing significant except that, in general, alkyds retain gloss longer than simple esters.

Table XIV-7 shows that linolenic esters and alkyds start peeling much sooner than corresponding linoleic compounds, and eleostearic compounds fall between. Peeling is not related to alcohol type. Table XIV-8 offers a slightly different measure of the same general property as Table XIV-7 and leads to the same general conclusion.

TABLE XIV-36
Project 24, Oxidation Studies: Maximum Diene Conjugation
Column *A:* Time required to reach maximum "diene conjugation," in hours.
Column *B:* Maximum conjugated diene absorption attained (absorptivity).

Type vehicle	Fatty acid component							
	Oleic*		Linoleic		Linolenic		Eleostearic	
	A	*B*	*A*	*B*	*A*	*B*	*A*	*B*
Glyceryl ester			4.5	30.3	1.0	18.1	2.0	34.9
PE ester	450	8.8	3.5	19.0	†	16.5	3.6	42.8
DiPE ester	355	9.4	4.5	22.4	1.5	13.7		
LO glycerol alkyd			3.5	13.7	4.0	12.0	‡	40.0‡
SO glycerol alkyd			5.0	13.0	1.5	7.0		
LO PE alkyd	180	4.5	2.4	14.4	3.6	14.4		
SO PE alkyd	90	3.4						

Varnish linseed oil		Dehydrated castor oil		Commercial alkyd	
A	*B*	*A*	*B*	*A*	*B*
2.4	13.5	‡	20.0‡	1.3	7.2

* Oleate compounds exhibited spectral absorption at 221 to 224 mμ and not in the conjugated diene region (232 mμ). It is not known how much of this absorption is caused by conjugated diene.

† No maximum value observed. Most highly oxidized sample had highest "conjugated diene" absorption after 7.5 hours.

‡ Highest "conjugated diene" absorption values were obtained *before* oxidation.

Project 9, Water and Alkali Tests

Only one deduction having statistical significance can be drawn from the three tables (XIV-11, XIV-12, XIV-13): the overall rating is poorest for oil esters, intermediate for long-oil alkyds, highest for short-oil alkyds. For all specific ratings of materials, tests, and times it can be concluded only that the differences between individuals are smaller than the rating errors or that each material behaved in a manner peculiar to itself.

Project 10, Yellowing

A preliminary analysis of the yellowing data on pigmented films at 50 days and at 385 days (Table XIV-14) revealed that time brought about no essential changes in order. Therefore the data for all times were combined to give the following results. Yellowing of

TABLE XIV-37

Project 24, Oxidation Studies: "Conjugated Diene" Present and Disappeared at Set Point

Column *A:* "Conjugated diene" at "set point" (mole per mole of fatty acid).*

Column *B:* "Conjugated diene" disappeared at "set point" (mole per mole of fatty acid).†

Column *C:* "Conjugated diene" disappeared at "set point" (mole per mole of vehicle).†

	Fatty acid component											
Type vehicle	Oleic‡			Linoleic			Linolenic			Eleostearic		
	A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
Glyceryl ester				0.24	0.49	1.47	0.18	0.23	0.69			
PE ester	—	—	—	0.20	0.44	1.76	0.16	0.18	0.72	—	—	—
DiPE ester	—	—	—	0.23	0.16	0.96	0.15	0.26	1.56			
LO glycerol alkyd				0.19	0.04	—	0.18	0.09		—	—	—
SO glycerol alkyd	—	—	—	0.29	0.42	—	0.15	0.33				
LO PE alkyd	—	—	—	0.32	0.77	—	0.17	0.47				
SO PE alkyd	—	—	—									

* Wheeler *et al.* (1) report molecular extinction coefficients of 27,400 for conjugated diene in *t*-9, *t*-11-methyl linoleate and 31,200 for *t*-10, *t*-12-methyl linoleate; since thermal oxidation at room temp. yields mostly *trans, trans* conjugation, the figure of 29,300 was taken for these calculations, which were made assuming that all the oxygen absorbed remained in the fatty acid molecule.

† The "conjugated diene" expected was calculated from the amount of "conjugated diene" formed when 0.05 mole O_2 per mole of fatty acid had been absorbed, assuming that this rate of "conjugated diene" formation with respect to O_2 absorption would remain constant throughout the experiment. The " 'conjugated diene' disappeared" is the difference between this calculated value and the observed values. Molecular alpha used, 29,300.

‡ Oleate compounds exhibited spectral absorption at 221 to 224 mμ and not in the conjugated diene region (232 mμ). It is not known how much of this absorption is caused by conjugated diene.

all esters and alkyds in either light or dark depends upon the nature of their acid constituent, increasing in the order oleic, linoleic, eleostearic, and linolenic. But although this order is the same for both light and dark aging, the level of intensities developed in the dark is considerably greater than in the light. Furthermore, the degree of yellowing reached in the dark is in direct relation to oil content, i.e., greatest for esters, least for short-oil alkyds; in the light this oil effect does not exist. It follows that the ratio of dark yellowing to light yellowing is also in direct relation to oil content. Yellowing and alcohol functionality are not related.

TABLE XIV-38

Project 24, Oxidation Studies: Triene Conjugation

Column *A:* Maximum "conjugated triene" attained (absorptivity).*

Column *B:* "Conjugated triene" accumulated at 1 mole O_2 per mole of fatty acid.

Column *C:* "Conjugated triene" disappeared at 1 mole O_2 per mole of fatty acid.†

Type vehicle	Fatty acid component											
	Oleic			Linoleic			Linolenic			Eleostearic		
	A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
Glyceryl ester				4.34	4.22	4.78	6.88	6.75	0.85	140.0‡	87.5	52.5§
PE ester	‖	‖	‖	3.75	3.62	6.49	6.98	6.25	5.45	153.3‡	30.5	122.8§
DiPE ester	‖	‖	‖	4.30	4.30	4.96	6.00	5.40	2.93			
LO glyc. alkyd				5.27	5.19	4.36	4.60	3.30	7.40	94.0‡	20.0	74.0§
SO glyc. alkyd				3.20	1.93	3.39	3.00	1.77	1.37	—	—	—
LO PE alkyd	‖	‖	‖	11.10	10.70	0.59	5.10	5.10	0.26			
SO PE alkyd	‖	‖	‖									

Varnish linseed oil			Dehydrated castor oil			Commercial alkyd		
A	*B*	*C*	*A*	*B*	*C*	*A*	*B*	*C*
4.00	4.00	6.60	2.9	2.25	12.75	2.75		

* Spectral absorption in the conjugated triene region (268 mμ) was insignificant in the case of the oleate compounds. With the linoleate compounds the spectral absorption observed in this region may be caused largely by conjugated diene ketones, whereas with the linolenates it probably results mostly from true triene conjugation.

† Expected "conjugated triene" was determined from "conjugated triene" formed at 0.05 mole O_2 per mole of fatty acid, assuming that this rate of "conjugated triene" formation would remain constant throughout the experiment. " 'Conjugated triene' disappeared" is the difference between the expected and the observed values, except for the eleostearates.

§ Difference between "conjugated triene" content of the unoxidized samples and the observed values for the oxidized samples.

‡ On unoxidized sample.

‖ No triene formed.

Omissions in the data for yellowing of clear films hindered the analysis, but in general the trends resemble those for pigmented materials. No comparison was made of pigmented vs. clear, since optical factors not related to the chemistry of the system would undoubtedly affect the level of results.

Projects 13 and 22, Erosion, Hardness, and Abrasion Resistance

Set-to-touch times as judged in this project were not precise enough to permit analysis. No conclusion could be drawn from the chalking data (Table XIV-15), but the accelerated weathering tests on pigmented films (Table XIV-16) gave linoleic alkyds an advantage over linolenic.

Weather-Ometer tests on pigmented films caused gloss deterioration (Table XIV-17) and weight losses (Table XIV-18) directly related to oil content, as is logical. In other words, esters lost most weight, lost luster faster; short-oil alkyds reversed this situation; and long-oil alkyds came between. Combining the Weather-Ometer results for clear and pigmented films reveals the further fact that linoleic alkyds retain gloss better than linolenic.

The average of Sward rocker tests for the paints at all ages (Table XIV-20) reveals, as expected, that hardness is inversely related to oil content; short-oil are harder than long-oil alkyds, and these in turn are harder than oils.

Excessive error and interaction obstructed general conclusions from the abrasion tests on the paints, but clear linolenic alkyds laid significantly harder films than linoleic. Effects of alcohol type and oil content were undetectable.

Ratings in Tables XIV-19 to XIV-22 for this project were obtained by transcribing the original data of Tables XIV-15 to XIV-21 to a rating system based on a scale of 0 = worst to 10 = best and combining them in related pairs or groups. From a statistical standpoint, this technique brought out no new information.

Projects 14 and 19, Permeability

The analysis of these projects provides an interesting example of the statistical method as applied throughout the present chapter. Thus, a purely intuitive examination of the data in Table XIV-23 for linoleic and linolenic esters might lead to the conclusion that

TABLE XIV-39. Summary of All Statistical Results

Project No.	Table	Measurement	Esters		Alkyds			Notes
			Acid effect	Alcohol effect	Acid effect	Alcohol effect	Oil effect	
1	XIV-1	Time to set (hrs.)	–	0	–	0	0	
	XIV-2	Gain in wt. to set-to-touch	0	0	0	0	+	
		Rate of gain	+	0	+	0	+	
	IV-30	Max. % gain with drier	0	0	0	0	+	
		Max. % gain without drier	+	0	0	0	+	
		Drier vs. no drier	*	*	*	*	*	Drier < no drier
	IV-31	Time of max. with drier	0	0	0	0	0	
		Time of max. without drier	–	0	0	0	0	
		Drier vs. no drier	*	*	*	*	*	No difference
	XIV-3	Sp. gr. with drier, 1 week	0	0	N	N	0	Insuff. data
		Sp. gr. with drier, 1 month	N	N	0	0	0	Insuff. data
		Sp. gr. with drier, 3 months	0	0	0	0	0	
		Sp. gr. without drier, 1 week	0	0	0	0	0	
		Sp. gr. without drier, 1 month	0	0	0	0	0	
		Sp. gr. without drier, 3 months	0	0	0	0	0	
		Rate increase of sp. gr. with drier	N	N	N	N	N	Insuff. data
		Rate increase of sp. gr. without drier	*	*	*	*	*	Rate is positive
		Sp. gr. value, all times	0	0	0	0	–	
		Sp. gr. value, drier vs. no drier	*	*	*	*	*	No difference
	IV-32	Set-to-touch time with drier	–	0	0	0	0	
		Set-to-touch time without drier	–	0	0	0	0	
	IV-33	Loss after baking, with drier	–	0	0	0	0	
		Loss after baking, without drier	–	–	0	0	0	
2	XIV-4	Atoms O_2/mole, 1 week	0	0	–	+	0	
		Atoms O_2/mole, 1 month	+	+	–	+	+	
		Atoms, O_2/mole, 1 year	0	+	–	+	0	
		Atoms O_2/mole, all times	*	*	*	*	*	Increases with time

3	XIV-5	% insol., 1 week	+	+	0	0	0	
		% insol., 1 month	+	+	0	0	0	
		% insol., 1 year	0	0	0	0	0	
		% insol., all times	*	*	*	*	*	Increases with time
4	XIV-6	Tensile strength	0	0	0	0	+	90% confidence
8	XIV-7	Start peeling, months, clear films	0	0	0	0	0	
		Start peeling, months, pigmented films	–	0	–	0	0	
	XIV-8	Peeling rating, 18 mo., clear films	0	0	0	0	0	
		Peeling rating, 20 mo., pigmented films	–	0	–	0	0	
	XIV-9	Weeks to lose 50% of gloss	0	0	0	0	0	
		Weeks for gloss rating to fall to 10–11	+	0	0	0	0	
	XIV-10	Weeks to first chalking	0	0	0	0	0	
		Weeks for chalk rating to fall to 6	0	0	0	0	0	
		Weeks for chalk rating to fall to 2	0	0	0	0	0	
9	XIV-11	Ratings 1950 water tests	0	0	0	0	0	
		Ratings 1951 water tests	N	N	N	N	N	Insuff. data
		Ratings both series, water tests	0	0	0	0	0	
		Ratings 1950 alkali tests	0	0	0	0	0	
		Ratings 1951 alkali tests	0	0	0	0	0	
		Ratings both series, alkali tests	0	0	0	0	0	
		Ratings overall, water and alkali	0	0	0	0	–	Error est. from all
10	XIV-14	Net yel. all times, light, pigmented	+	0	+	0	0	
		Net yel. all times, dark, pigmented	+	0	+	0	+	
		Ratio: dark/light, pigmented	0	0	0	0	+	
13	VII-1	Set-to-touch time, clear	N	N	N	N	N	Data inadequate
	VII-2	Set-to-touch time, pigmented	N	N	N	N	N	Data inadequate
	XIV-15	Chalking	0	0	0	0	0	
	XIV-16	Accel. weath., time to fail, clear	0	0	0	0	0	
		Accel. weath., time to fail, pig.	0	0	–	0	0	
	XIV-17	Gloss retent., W'Ometer, clear	0	0	0	0	0	
		Gloss retent., W'Ometer, pig.	0	0	0	0	–	

(continued)

Table XIV-39 (*continued*)

Project No.	Table	Measurement	Esters		Alkyds			Notes
			Acid effect	Alcohol effect	Acid effect	Alcohol effect	Oil effect	
	XIV-17	Overall rating on gloss retention	0	0	–	0	0	
	XIV-18	Wt. loss 6 hr. W'Ometer, clear	0	0	0	0	+	
		Wt. loss 12 hr. W'Ometer, clear	0	0	0	0	0	
		Wt. loss 6 + 12 hr. W'Ometer, pig.	0	0	0	0	+	
	XIV-19	Appearance	0	0	0	0	0	
	XIV-18	Overall rating on weight loss	0	0	0	0	0	
22	XIV-20	Sward hardness, 8 days, clear	N	N	0	0	0	Insuff. data
		Sward hardness, 3 months, clear	N	N	0	0	0	Insuff. data
		Sward hardness, 8 days, pig.	0	0	0	0	N	Not computed
		Sward hardness, 3 months, pig.	0	0	0	0	N	Not computed
		Sward hardness, all times, pig.	0	0	0	0	–	
		Overall rating on Sward hardness	0	0	0	0	–	
	XIV-21	Abrasion coef., clear	N	N	+	0	0	Insuff. data
		Abrasion coef., pigmented	0	0	0	0	0	
		Overall rating on abrasion resist.	0	0	0	0	0	
	XIV-22	Overall rating, Projects 13 & 22	0	0	0	0	–	
14	XIV-23	Permeability constant, vapor	0	0	0	0	0	
	XIV-24	Permeability constant, liquid	N	N	0	0	N	Insuff. data
16	XIV-25	Molecular area at 0 pressure	0	+	0	0	–	
		Molecular area at crumpling pressure	0	+	0	0	–	
		Above combined	+	+	+	0	–	
	XIV-26	Force at crumpling point	0	0	0	0	+	
		"x" values in equation of state	0	0	0	+	+	
17	XIV-27	Acid value, clear, 4 weeks	0	0	0	0	0	
		Acid value, clear, 16 weeks	0	0	0	0	0	
		Acid value, pigmented, 4 weeks	0	0	0	0	0	
		Acid value, pigmented, 16 weeks	0	0	0	0	0	

		Combined acid number data	–	0	0	0	+	Linoleic > $\left\{\begin{array}{l}\text{oleic}\\\text{linolenic}\\\text{eleostearic}\end{array}\right.$
	XIV-28	Sapon. value, clear, 4 weeks	0	0	0	0	0	
		Sapon. value, clear, 16 weeks	0	0	0	0	0	
		Sapon. value, pigmented, 4 weeks	0	0	0	0	0	
		Sapon. value, pigmented, 16 weeks	0	0	0	0	0	
		Combined sapon. value data	0	0	0	0	0	
	XIV-29	Mg. ZnO in washings, 12 weeks	0	0	0	0	0	
		Mg. TiO_2 in washings, 12 weeks	0	0	0	0	0	
21	XIV-30	Max. refractive index, clears	0	0	0	0	0	
24	XIV-31	Hrs. to absorb O_2/mole F.A.	–	0	0	–		
		Initial rate O_2 absorption	0	0	0	0	0	
	XIV-32	Hours to set	–	–	0	0	0	
	XIV-33	O_2 absorbed at set pt./mole F.A.	0	0	0	0		
		O_2 absorbed at set pt./mole veh.	0	0	0	0		
	XIV-34	Hrs. to reach max. peroxide	0	0	0	0	0	
		Max. peroxide, moles/mole F.A.	0	0	0	0	0	
	XIV-35	Ratio peroxide/O_2 at set	0	0	–	0	0	
		Perox. content at 1 mole O_2 abs.	0	0	0	0		
		Perox. disappeared/hr.	+	0	0	0		
	XIV-36	Hrs. to max. conj. diene	N	0	0	0	0	One max. lacking
		Max. conj. diene attained	0	0	0	0	+	
	XIV-37	Conj. diene at set pt./mole F.A.	–	0	0	0		
		Conj. diene at set pt./mole veh.	0	0	N	N		Insuff. data
		Conj. diene disappeared at set/F.A.	0	0	0	0		
	XIV-38	Max. conj. triene	+	0	0	0	0	
		Conj. triene at 1 mole O_2/F.A.	+	0	0	+		
		Conj. triene disappeared at 1 mole O_2/mole F.A.	0	0	0	0		

Key: + and – indicate positive (direct) and negative (inverse) relationships as defined in the section on Methods (pages 356 to 365); 0 indicates that analysis of the data showed no significant relationship; * signifies that data for all materials were combined to apply a test for a special property or relationship; N means that analysis was impossible for reason given in note.

linoleic oils *in general* are more permeable than linolenic. This, of course, would be a most interesting result but unfortunately it cannot be confirmed by statistical findings as any more than 75% probable, which is not ordinarily acceptable. Likewise, there is no detectable general relationship between oil content and permeability. The fact that almost every datum tabulated is the average of several measurements does not alter these conclusions and, in fact, the one value in the table (trilinolein) which most strongly influences the statistics is the result of a single measurement. Even if it were to be assumed that every number in the table is absolutely precise and accurate, the best that statistics could do would be to conclude that each compound behaves in a manner peculiar to itself. Identical remarks apply to Table XIV-24 on liquid permeability.

Project 16, Molecular Size, Shape, and Weight

On considering separately Columns A and B of Table XIV-25, the difference in size between linoleic and linolenic materials does not quite meet the 95% confidence standard. On combining the two columns, however, the standard is easily met and linolenic compounds are shown to have greater cross-sectional area than their linoleic counterparts. At either of the two pressures, F_0 and F_c, used in the measurement (and in the combined table) the areas of oil esters are directly related to alcohol functionality; this relationship fails with alkyds. It is also apparent that area at both pressures is inversely related to oil content. The force at crumpling point and the "x" values (Table XIV-26) appear to have no particular dependence on acid or alcohol type, but both are directly related to oil content. All these findings fit into the expectation that complex molecules (resins) should have a larger cross section than simpler ones (oils), and the latter form a more compact film structure which is harder to crumple.

Project 17, Acid and Saponification Numbers

No general trends of acceptable confidence could be discerned in any of the individual tables (XIV-27, XIV-28, XIV-29) of this project. By combining the columns for acid number, however, linoleic esters emerged as possessing somewhat higher values than those of oleic, linolenic, and eleostearic acids. This applies to clear and pigmented esters but not to alkyds. Since no other relationship to structure could be detected, it must be concluded that each material acts in a manner peculiar to itself or that the techniques of measuring acid and saponification numbers cannot detect small differences. Probably both of these factors are involved.

Project 21, Refractive Index

No general relationship to structure was found (Table XIV-30), except, of course, that conjugated materials had higher values than nonconjugated.

Project 24, Oxidation Studies

The complex nature of the work undertaken in this project made some of the results suffer in the attempt to reduce them to simple tabular form for statistical treatment. Nevertheless a number of fairly clear-cut relationships were discernible; these are presented with no attempt at interpretation.

The time taken by linolenic esters to absorb 1 mole of oxygen per mole of fatty acid (Table XIV-31) is distinctly less than for their linoleic counterparts. The expectation that faster oxygen absorption would result in shorter setting time is borne out by Table XIV-32; both findings agree with conclusions reached in Project 1. Concentration of conjugated diene at set (Table XIV-37) is greater for linoleic than for linolenic esters. On the other hand, the rate of peroxide disappearance up to the setting point (Table XIV-35), maximum conjugated diene concentration (Table XIV-36), and the conjugated triene when 1 mole of oxygen had been absorbed per mole of fatty acid (Table XIV-38) are all greater for linolenic than for linoleic oils.

In three instances oxidation proved its relationship with alcohol functionality: (*1*) The time to absorb 1 mole of oxygen per mole of acid varies inversely with alcohol functionality for alkyds. (*2*) The setting time varies inversely with alcohol valence for esters. (*3*) The concentration of conjugated triene, when oxygen absorption reached 1 mole, increases with alcohol functionality for alkyds. Only one example of a relationship to oil content came to light; this was in the maximum conjugated diene attained (Table XIV-36). Undoubtedly, many of the other properties are similarly related to oil content, but as almost all the data were expressed in terms of 1 mole of fatty acid, the relationship was not sought.

Some of the general correlations between the findings of diffierent projects have been mentioned here; others, based on everyday reasoning rather than on statistical treatment, will be discussed in the next chapter.

References

1. Jackson, J. E., R. F. Paschke, W. Tolberg, H. M. Boyd, and D. H. Wheeler, *J. Am. Oil Chemists' Soc., 29,* 229 (1952).
2. Youden, W. J., *Statistical Methods for Chemists.* Wiley, New York, 1951.

CHAPTER XV

Summary of Correlations and Evaluations

As in the statistical study described in the previous chapter, the common-sense correlation and evaluation of data was limited by the fragmentary, and sometimes contradictory, nature of the results from several of the projects. Members of the Evaluation Committee searched diligently for all clues that might lead to the unearthing of causes and effects. What they found in the data of the particular projects assigned to them, without regard to others, has been included in the discussions in Chapters IV to XIII. Each member sought also to find all the possible relationships of his assigned project with all the other studies. Thus their studies overlapped and included many repetitions; in consolidating their reports, the editor has tried to avoid most of the repetitions without omitting anything of value. Careful students will undoubtedly find additional grounds for valid deductions hidden here and there in the data.

Project 1, Gain in Weight, showed in general the expected results, and data from other projects fall mostly in line. However, the actual oxygen content of dried films as found in Project 2 is substantially greater than can be accounted for by direct absorption of oxygen in the amount measured by weight gain. From other projects, too, it appears that decomposition or scission products, some of which are volatile and escape from the film while others remain, must be involved, in a ratio which depends upon the thickness of the film. Film thickness, thus, has a strong influence upon behavior; and in spite of the care taken to eliminate this as a disturbing variable, differences were undoubtedly sufficient to account for some of the anomalies observed.

Setting and drying times as recorded in Project 1 follow very nearly the same order as in the other projects where they were noted, although actual times varied somewhat at different locations.

Project 3, Solvent Extraction, showed losses in solubility on aging roughly in accordance with gain in oxygen content. Linolenic compounds scored highest in both extraction residue and oxygen gain, although eleostearates started off faster. Monomeric oil substances lower in unsaturation add oxygen and gradually join into linear polymers, which in turn cross-link together into relatively large-sized units. Monomers of higher activity polymerize faster if oxygen can find its way to the unreacted molecules, and form less soluble films. A fully polymerized film is essentially insoluble in boiling carbon tetrachloride, but this state may be reached finally only after years of curing under the conditions of these tests.

Project 4, Distensibility, was a study of mechanical properties, and its relation to the only other project of that class (Project 22, Hardness and Abrasion Resistance) was briefly noted in Chapter XI. There were some studies on chemical properties which could conceivably have a connection either with absolute tensile behavior or with its change with time. Scofield's work on gain in weight covered time periods from a few hours to about 13 weeks—nearly the same as for most of the stress-strain measurements. He found that the maximum weight increase of clear films containing drier is independent of film composition within the limit of experimental error. This conclusion is in general agreement with the distensibility measurements in predicting small relative differences in aging rate of the various compounds.

Following the same line of reasoning, it is logical to expect that the change in oxygen content of drying oil films on aging might reflect the same structural changes which produce the decrease of distensibility. The data of Table XV-1 are computed from Williams' ultimate analyses (Project 2):

TABLE XV-1

Ratio of Oxygen Content to Content of Double Bonds (Mole per Mole)

Compound	1 Month	1 Year
Trilinolein	1.1	1.2
Trilinolenin	1.0	1.0
Trieleostearin	0.9	1.0
PE linoleate	0.9	1.2
PE linolenate	0.7	0.8
PE eleostearate	0.9	0.9
LO linoleic glycerol alkyd	1.1	1.8
LO linolenic glycerol alkyd	0.8	1.4
SO linoleic glycerol alkyd	1.1	1.8
SO linolenic glycerol alkyd	0.7	1.5

There may be some significance to the fact that linolenic materials invariably show a smaller ratio than linoleic counterparts, but the existence of a similar relationship among the μ values for alkyds (Table XI-3) is probably coincidence. The changes in oxygen content between one month and one year are more important. For alkyds these are fairly substantial, and they parallel equally substantial losses in distensibility of alkyd clears during the same interval. But for esters the changes in oxygen content were nil and during this time the stress-strain properties were undergoing changes so small and erratic that distensibilities could not be obtained. It may also be important to note that the systematic decreases in distensibility took place primarily when the oxygen content exceeded the value of 1 mole per mole of double bonds.

In all the foregoing, it is of course recognized that oxygen content and oxygen uptake are distinctly different quantities. Williams thought that the evolution of volatiles was small; if so, oxygen uptake measurements should lead to essentially the same conclusions. For the most part, Chipault's data (Project 24) on oxygen uptake covered only the period up to 100 hours; hence extended aging effects cannot be compared with distensibility. It is interesting to note, however, that for linolenate compounds oxygen absorption had practically stopped by the end of 3 days, whereas it was still going on at a slow but steady and substantial rate in linoleates and eleostearates. This tends to confirm the evidence of Table XV-1 to the effect that linolenate materials never reach the relative level of oxidation attained by linoleates and eleostearates. So far as concerns individual compounds, no reliable or systematic correlations can be drawn between oxygen absorption data up to 100 hours and changes occurring later in mechanical properties. In general, Williams' and Chipault's data complement each other in suggesting that oxygen taken up in the first few days or weeks of exposure would be sufficient to explain mechanical degradation by light, even if the specimens were to be placed in an inert gas after the initial period.

Since the solubility of a polymer in organic solvents serves as a rough measure of cross-linking, it is reasonable to look for a correlation between solubility and mechanical behavior. However, the extraction of films with carbon tetrachloride at various ages in Project 3 shows no significant correlation with structure, only the concomitant decrease of both solubility and distensibility with time.

The data of Project 5, Absorption of Organic Liquids (by extracted films), are too erratic to permit comparison.

Direct correlation between infrared readings of Project 6, Spectrophotometric Measurements, and the findings of other projects is impossible because of the limited number of samples examined and because of the fact that the samples were dried without drier (so that changes would be slowed down to permit observation). The ultraviolet data are likewise scattered; there is, however, good agreement between the data of this project and those of Project 24.

Project 8, Exterior Exposure Tests, corresponded fairly well with the accelerated weathering results of Projects 13 and 17, especially in the case of linoleic and linolenic compounds. Too much dependence cannot be placed on incidence of peeling, because of probable impairment of adhesion as discussed in Chapter I, but it may be significant that the films of clear and pigmented linolenic compounds, which absorbed oxygen faster and to a higher content in Projects 2 and 24, chalked and peeled faster than the linoleic.

Films which showed best resistance to water and alkali in Project 9 chalked less (although dehydrated castor oil and LO linoleic PE alkyd, with poor water resistance, took 15 weeks to reach a chalk rating of 2), and in general peeled more readily. They were also, on the whole, the hardest films in the Sward rocker test of Project 22.

Project 9, Water and Alkali Tests, demonstrated in the combined ratings roughly comparable resistance to these reagents and to attack by carbon tetrachloride (Project 3). Chief exceptions were the PE and diPE linolenates with poor water and alkali ratings and very low solubility, and the commercial alkyd, where the reverse was true. In general it appears that, other things being equal, higher molecular weight due to more cross-linking in the film (as reflected by low solubility) imparts better water and alkali resistance.

In Project 17 the amount of zinc oxide leached from pigmented films was usually low for those vehicles with high water and alkali ratings, yet the eleostearic compounds with low ratings showed negligible leaching. High Sward hardness pointed, with exceptions and reversals, toward increased resistance to these reagents.

Permeability to water and to water vapor (Projects 14 and 19) might reasonably be expected to parallel water degradation of films, but the data show no indication of this.

Project 10, Yellowing, concerns a phenomenon that is closely associated with spectral absorption changes, and with increase of conjugated unsaturation resulting from oxygen absorption. Hence, the discussion in Chapter VIII has already covered some of the correlations between the data of this project and those of Projects 1, 2, 6, and 24. Lower oil contents, and in some cases slightly lower levels of oxidation, in the alkyds probably account for differences between them and the esters. Differences between light and dark aging may be due to actinic light effects in causing destruction of the chromophores, as in the fading of dyes.

Of the projects in the program other than those mentioned above, few showed any positive correlations with yellowing and even these, not in the sense of cause and effect. Certain properties of linolenic compounds as compared with linoleic (such as solvent resistance, general hardness, rate of oxygen absorption) seem logically attributable to a slightly greater reactivity of the linolenic structure, rather than to any direct connection between yellowing and any of the other individual properties. It is interesting to note that whereas an especially high reactivity often has been postulated for the two doubly activated methylene groups of the linolenic radical (and also for the conjugated arrangement of the eleostearic radical), the majority of properties studied in the program show no reliable dependence on their presence.

Gloss changes of Project 12 were limited to readings on panels exposed indoors in the dark, and they brought out no interesting correlations with even those projects in which incidental readings of gloss were made, on films subjected to exterior or accelerated weathering.

Set-to-touch time of vehicles with drier, as recorded in Project 13, Erosion, came somewhat later than in Project 1, but the pattern was essentially the same. Weight loss in the Weather-Ometer corresponded roughly to weight loss after baking, except for LO linolenic glycerol alkyd, which lost little in weathering but relatively much on baking. Low weight gain seemed generally to parallel good resistance to erosion.

Gloss retention in the Weather-Ometer was much better for alkyds than for esters; on exterior exposure (Project 8) differences were much less and were variable. Chalking of pigmented films by the two methods was roughly alike in order, although in the accelerated test linolenic compounds resisted better than they did outdoors.

There was very poor correlation on peeling; film failure appeared to progress by different paths under the two exposure systems, as has frequently been noted in comparing such data.

The numerical rating averages for erosion, hardness, and abrasion resistance shown on page 207 were set for comparison alongside the combined ratings (see page 244) assigned for water and alkali tests of Project 9:

	Water and alkali	Erosion, etc.
SO linoleic glycerol alkyd	7.7	8.2
LO linoleic glycerol alkyd	7.7	7.4
Commercial alkyd	7.5	7.2
SO linolenic glycerol alkyd	6.7	6.9
SO oleic PE alkyd	6.	6.8
LO linolenic glycerol alkyd	8.7	6.2
LO linolenic PE alkyd	5.0	6.0
LO linoleic PE alkyd	4.5	5.4
LO eleostearic glycerol alkyd	8.2	5.3
PE linolenate	3.0	4.6
Trilinolenin	4.2	3.8
DiPE linolenate	3.0	3.6
LO oleic PE alkyd	4.0	3.0
PE eleostearate	3.0	2.9
DiPE linoleate	4.7	2.4
Trilinolein	2.2	2.2
Varnish linseed oil	2.0	2.0
Trieleostearin	3.0	1.7

The table indicates rather good correlation, with a few evident exceptions.

Permeability to water vapor paralleled loss of gloss and weight loss in the Weather-Ometer and softness in the rocker and abrasion tests, especially for trilinolein, diPE oleate, and linseed oil.

No correlation was established between erosion, hardness and abrasion resistance, and the data of Project 16 (Molecular Size, Shape, and Weight), other than that compounds of highest molecular weight (alkyds) performed best in these tests.

Gloss retention was better for those esters which in the oxidation studies of Project 24 absorbed oxygen fastest; but this did not hold true for alkyds. The same relationship between the total rating for erosion, hardness and abrasion resistance, and oxygen absorption holds also for the esters but again not for the resins.

Some relations of permeability measurements (Projects 14 and 19) to other studies have already been mentioned; others will follow.

Project 16, Molecular Size, Shape, and Weight: Good general correlation is found wherever the size of the molecule is expected to be controlling: rate of weight gain and oxygen absorption, loss of solubility, resistance to water and alkali, etc.

Although Project 11, Adhesion, was not carried out, Dr. Long in his evaluation of Project 16 advanced the concept that F_c, the force at the crumpling point of the monomolecular film, is the fundamental true measure of adhesion to water and hence, substantially, of adhesion to water-loving surfaces, including wood, masonry, and metal. With limitations and reservations, his idea assumed that when the film crumples and the molecules pile up into multilayers, the force at that instant is the force required to pull molecules away from the plane water surface and exactly equals the force of adhesion. Constants can be found for specific surfaces as compared to water. A paper (1) by Bobalek and LeBras refers to this concept; and Dr. Long elaborated his thinking in the Mattiello lecture of 1954 (2).

In comparing molecular dimensional factors with permeability, he noted that, except in the case of trilinolein, films of the natural oils were more easily penetrable by water vapor than the pure compounds. This suggested that permeation is favored not only by the presence of the softer, more saturated oleate radicals but also by random orientation where dissimilar molecules make up the barrier. When the molecules are all alike, the film may be denser in the sense that the spacings and linkages are more uniform—an effect like a phalanx formation of soldiers. As already noted, increasing molecular weight in the alkyd series reduced permeation (which was 1.75 for LO linoleic glycerol alkyd, mol. wt. 2445, but only 0.82 for SO linolenic glycerol alkyd, mol. wt. 5028).

Film shrinkage as studied in Project 20 increased the density of natural oils from 0.93 originally to 1.12 after 160 days, of PE and diPE esters to 1.20, and of trieleostearin to 1.117. The molecular area measurements showed that it takes 19.6 dynes per centimeter to crumple trieleostearin films, against 8.9 for trilinolenin. Progressive compaction of the aging film, seen by Carrick and Permoda as causing increases in specific gravity, is evidently resisted by the more quickly developed cross-linking of the trieleostearin film.

In Project 17, Chemical Changes, the only determinations made on the films exposed in the Weather-Ometer were those of acid and saponification values. The results, especially on the latter, were too erratic for detailed correlation with those of other projects, even where the nature of the study and the uniformity of time period (1 to 16 weeks) might have permitted. There is a vague parallelism between formation of peroxides, hydroxy groups, and diketones, as indicated by some of the other studies and the gradual, though highly irregular, increase in acid and saponification values.

Project 18, Depth of Oxygen Penetration, definitely proved that film thickness is a determining factor in the uptake of oxygen and that oxygen content decreases from top to bottom of the film. This fact explains the difficulty of correlating values obtained from film studies with other physical and chemical observations. It confirms the suggestion of Project 16 that further studies of monomolecular films should be made.

Project 20, Film Shrinkage, indicated almost uniform decrease in volume with aging (for the seven materials tested), in spite of variations in total weight gain and, to a less extent, in density.

Refractive Index Measurements of Project 21 could be made only for limited periods varying from 5 minutes to 10 hours (16 days for oleic esters); thus correlations are limited. Oxygen absorption and development of diene and triene conjugation would be expected to raise the index, and a plot of index readings against per cent increase in weight (Fig. XV-1) conforms with this for those compounds the refraction of which increased in a regular manner.

Project 22, Hardness and Abrasion Resistance, has been compared, where possible, with other data in the foregoing.

Project 24, Oxidation Studies, helped greatly to bring the total picture of the research into good focus, as will be seen from glancing at correlations with individual projects.

Rates of oxygen uptake correspond closely with rates of weight gain (Project 1). Linolenic oils absorbed a little more oxygen and attained a somewhat higher maximum peroxide value than linoleic, consistent with a slightly larger gain in weight. The steady decline in peroxide content after a maximum was reached corresponded with a loss in weight of films due to volatilization of decomposition products and further oxidation of peroxides. In general, results of the ultimate analyses of Project 2 were also consistent with oxygen absorption and peroxide accumulation data.

The solubility studies of Project 3 were consistent with the interpretations of the polymerization reactions based on the results of Project 24. In particular, the linolenates which lost solubility most completely and in shortest time also attained highest absorption levels. On the basis of the deductions from the spectral curves, they polymerized fastest and to the greatest extent.

Decrease in distensibility (Project 4) parallels to an appreciable extent the loss in conjugated diene and other chemical changes that occurred in linoleate and linolenate films. Such a decrease would be expected, as condensation reactions and those of conjugated diene groups brought about further polymerization. These changes are also consistent with decreased solubility.

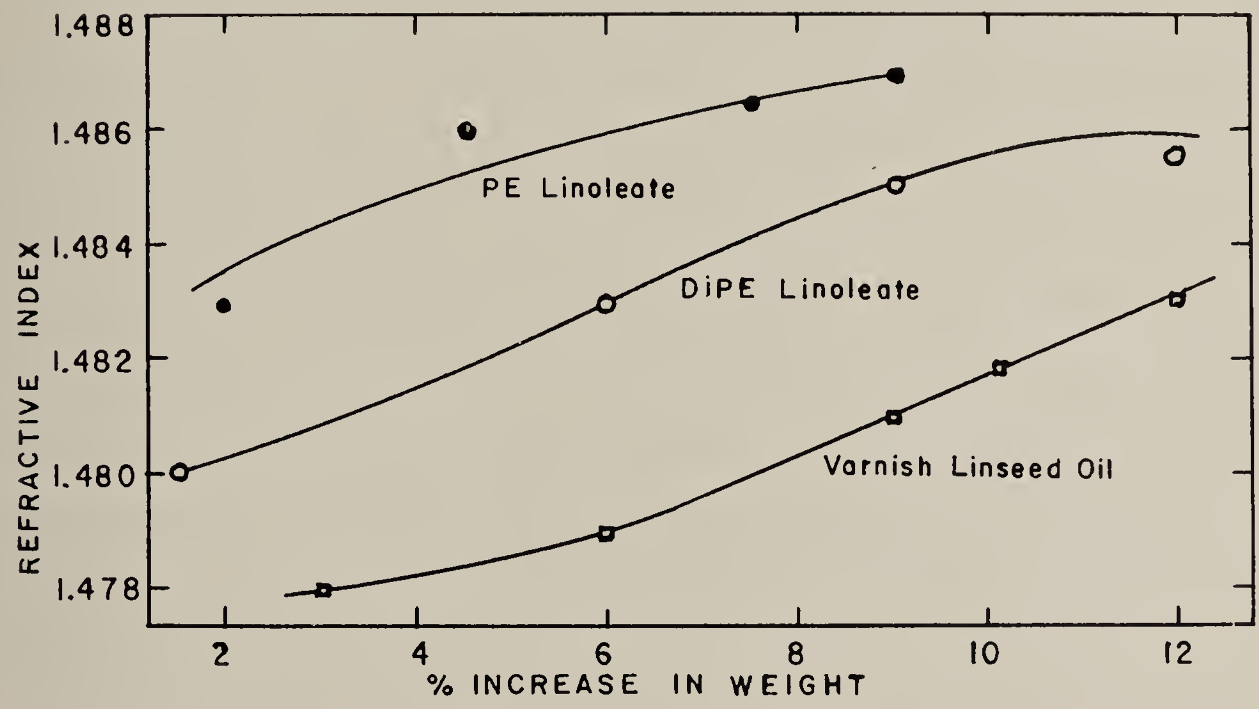

Fig. XV-1. Relation between refractive index and gain in weight of films.

The infrared and ultraviolet spectral measurements, made directly on oxidizing films in Project 6 and on products of reduction and hydrolysis in Project 24, are in good agreement where comparable, confirming the validity of both types of measurement. There is genuine need for both techniques, for neither meets all conditions. Direct measurements on the film may outrange the spectrophotometer, and they require very thin films; reduction and hydrolysis may lead to considerable errors in films aged appreciably beyond the set point.

That, in Project 8, the linolenic films chalked and peeled faster than linoleic is explained by their higher oxygen absorption. Also, the poor performance of the special compounds on exterior exposure as compared with commercial vehicles is consistent with their marked deviation from an "ideal" or average functionality. The unexpectedly rapid failure of the eleostearic vehicles, in spite of low oxygen uptake, may readily be accounted for by their lack of gas-proofness, along with the oxidation of unpolymerized eleostearate radicals, which in Project 24 was found to continue for an extended period of time.

Although there are some apparent inconsistencies between the results of Project 24 and those of Project 9, there is good correlation between the maximum peroxide content attained and the quality ratings of the water and alkali tests. Compounds earning the highest of these ratings, notably the long- and short-oil glycerol alkyds, had the lowest peroxide maxima. The long-oil PE alkyds and the simple esters, with higher peroxide maxima, rated low in quality.

Particular interest attaches to the yellowing tendencies and ultraviolet spectral data of Project 24. The stronger color assumed by linolenic than by linoleic compounds in the dark conforms with stronger absorption in the conjugated triene region of the spectrum. Such absorption is known to be due in part at least to conjugated diene ketones and other types of carbonyl compounds, where double bonds between adjoining pairs of atoms offer sites for resonance. It is also known that such structures may condense to form yellow quinone derivatives, of which even trifling amounts can impart an appreciable amount of color.

In spite of relatively low oxygen content, the eleostearates also yellowed considerably. However, only a little of the oxygen they did absorb appeared as measurable peroxides. Here again, other types of oxygenated derivatives could have formed which were themselves colored or could condense to form colored compounds.

The higher degree of yellowing in darkness is not easily explained on the basis of the results of Project 24. It is known that light accelerates autoxidation reactions in unsaturated fatty acid esters but there is no change in basic mechanism, at least initially; a difference in products of secondary reactions must be involved.

Gloss, as affected by type of fatty acid, corresponds to some extent with oxygen absorption or maximum peroxide content, but direct relationship was not found. Nor did additional significant correspondences appear in the results of tests of erosion, hardness, and abrasion resistance.

Permeability to water and to water vapor might be expected to be assisted by the greater solubility of H_2O molecules in more highly oxidized, hence more polar, films. However, the stronger barrier opposed by linolenate than linoleic esters to passage of water molecules indicates that the degree of compactness of structure due to cross-linking has an overriding effect. This same structural rigidity seems to account for the greater loss of distensibility of the linolenates.

Other projects (16, 17, 18, 21) cannot be compared directly with Project 24 because conditions differed too greatly. As to the almost uniform shrinkage values of Project 20 (all readings of which were at greater ages than those of the oxidation studies), it may be said that oxidation of the films is observed to continue for long periods of time and that ultimate degradation may reach approximately the same limiting value without regard to original composition, thus yielding polymeric residues the volume of which is roughly comparable in most cases, although their chemical structures may vary greatly.

Thus, on the whole, mosaic pieces of the Film Project fit together fairly well to bring out a picture, as Dr. Long and his fellow members of the Educational Committee had hoped. With many of the fragments missing, and others of not quite the proper shape, the picture has more of the massed, blurry effect popular with the modern school of painting than of the precise, detailed outlines favored by the classical school. It is, in any event, a notable addition to the world's gallery.

One of its worth-while by-products was the stimulation of studies in the organic coatings field by a number of university and other groups not previously interested in such investigations. The participation by so many cooperators in a country-wide community effort inspired new enthusiasm throughout the Federation for the work of advancing the frontiers of knowledge on coating behavior.

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CHAPTER XVI

Suggestions for Future Work

An exploration of unknown fields, especially one as ambitious and far-flung as this film study, was bound to meet with obstacles and disappointments. But whereas on some paths it ran into dead ends or failed to lead to expected goals, on others it either reached these goals or opened up very promising new territory for further exploration. It was valuable, too, in pointing out needed improvements in methods for future studies along similar lines. Many of the same projects are well worth taking up at the point where the Federation teams had to break off. Some of them had scarcely gone beyond the stage of developing satisfactory new techniques; others had not even reached that stage.

In these future studies, the Evaluation Committee suggested that the program should be more closely knit and integrated. While the groups working on each project might advantageously be larger, there should be fewer of them. They should work with fewer compounds but have larger quantities of each to permit determinations on a greater variety of properties and with more replication. All studies should be so designed as to permit reliable statistical analysis.

An important unanswered question from Projects 1 and 2 is why the total oxygen content in dried films is greater than the sum of that in the original molecule plus the gain in weight on drying. If the volatile products of the drying reaction are chiefly water and carbon dioxide, as is usually assumed, the discrepancy is even harder to explain because they would carry off more oxygen than hydrogen and carbon. A study of the compounds given off by drying films, to determine whether any hydrocarbons are present, should help to clear up this mystery.

Mechanical properties are among the most fundamental characteristics of surface coatings, and even the limited success attained in the present program should be an encouragement to continue. During the past few years, mechanical properties of elastomers and textiles have received a vast amount of attention, leading to hundreds of publications. Surface coatings, which in many respects are much less tractable substances, have received so little attention that the fundamental work by Elm may still be regarded as a pioneering effort.

Some of the interesting problems for future stress-strain studies were pointed out by Elm (1) in his 1953 Mattiello lecture. They included effects of pigment size, shape, and chemical composition, among many others. The most pressing problem of all, however, is the study of the technique itself. Time and money must be spent in determining which properties should be measured, which ones can be measured, and how to measure them accurately and reproducibly. The second step must consist of learning how to treat the experimental data in such a manner as to obtain and deal with fundamental properties of matter rather than geometrical peculiarities of specimens.

The same thorough overhauling of techniques is needed for studies of abrasion resistance, hardness, and adhesion. This last is such an important property in itself and bears so directly on other measurements that it should receive special attention.

In this connection, exterior exposure tests, as in Project 8, should certainly be a part of any future program of this type. But uncertainty about the influence of wetting properties upon the adhesion of the films suggests that precautions should be taken to assure a good bond between the films and their substrates. If proper adhesion cannot be attained in other ways, perhaps it could be (*1*) by adding a wetting agent to the compounds, (*2*) by preheating the panels and avoiding condensation of moisture or fumes upon them until the film is cast, (*3*) by using ground or etched glass plates, or panels of various metals, carefully cleaned. With sufficient replicate tests (preferably including some exposed under different climatic conditions), more dependable data on the influence of structure upon weather resistance can be obtained. The same remarks apply to accelerated exposure tests, for the measurement of erosion, peeling, and other changes.

The water and alkali tests suffered greatly from the lack of an objective or numerical basis for recording results. The cooperators made a good start toward filling this gap, but still better methods of judging results, when developed, could differentiate more closely between vehicles of varying composition. Although no great amount of illumination on the fundamental changes in films is likely to be shed by tests of this type, they are of real practical value.

Satisfactory measurements of both permeability and porosity depend on the laying of films of perfectly uniform thickness and of means for duplicating successive readings. Effective studies of methods of attaining these objectives would contribute greatly to more useful data, and perhaps give information on arrangement of molecules in the film. Another source of such information might be a study of extraction of films of increasing ages by several different organic solvents. This study could be limited to a few compounds, drawn down in graduated thicknesses and dried under varying conditions.

In extending the investigation of molecular size, shape, and weight, it might be of interest to obtain data on the rate of oxidation of monolayers of unsaturated fatty acids, of drying oils, and of single-acid esters, like the Federation compounds, by the methods of surface pressure and phase boundary potential developed by Gee and Rideal (2) at Cambridge University in England. This new approach might coordinate oxidation with molecular structure as a function of monolayer orientation. It could possibly yield fundamental information on one aspect of the drying process. Results of Project 18 on depth of oxygen penetration reinforce this suggestion.

If means can be found of reading accurately and with good reproducibility the crumpling point for air-exposed films (in Project 16 it lost sharpness at about 15 minutes exposure), force-area measurements of more compounds and at longer aging times should produce significant data on the rate and extent of monolayer oxidation. Compared with those on oxidation of thicker films, and on oxidation in bulk, they might clear up some of the present uncertainties. Studies of ether derivatives, as well as esters, of the acids used in this investigation should also be worth while.

It would seem that procedures might be found which would yield consistent, reproducible acid and saponification numbers and thus permit the drawing of well-supported conclusions therefrom.

Exact identification of the chromophores which cause the yellowing of films of drying oils and alkyds is handicapped by two great obstacles. The first of these rests in the fact that the amount of such materials required to produce yellowing is probably very small, and even worse, the chromophoric groups are usually tied into an insoluble cross-linked resin structure from which they cannot be removed without risk of destruction or, what would be equally undesirable, without the formation of new chromophores not present in the original film.

Chromatographic and polarographic analysis of extracts from yellowed alkyd films has shown some promise. This approach might be tried with profit on model compounds the oxidation products of which would be more likely to remain soluble. Effects of pigments could also be studied in this way.

Future studies of yellowing might also include exposure of panels, some freshly coated and some after they have yellowed strongly in the dark, to direct sunlight rather than merely to normal room illumination. It is known that sunlight has a bleaching effect on some yellowed films but there is little quantitative evidence. The same specimens may show gloss changes of somewhat different character than could be read from the dark-exposed panels measured for this characteristic in Project 12.

The oxidation studies of Project 24 led to some suggestions bearing not only on possible extensions of that work but also on the whole situation as disclosed by the Federation program. To determine precisely what happens during the oxidation of oils and to provide information that will aid in the formulation of better protective coatings, research is needed along the following lines.

1. It is evident from the disparities in the comparative rates of oxidation in relation to unsaturation between oxidation in bulk and in thin films, that some type of surface effect plays an important role in the latter case. This effect may partly influence not only the kinetics, but also to a considerable extent the nature, of the products, including the structures of the oxidative polymers. Researches should be conducted to determine the nature and importance of such phenomena.

2. During passage from a tacky to a tack-free film a slight decrease was observed in the average molecular weight of the fatty acid residues from the reduced and hydrolyzed film. The significance of this decrease in relation to polymer formation, if any, should be determined.

3. Better methods for analysis of oxidized films are needed. In particular, a suitable way to measure ether linkages accurately should be devised. Improved procedures for the determination of hydroxyl number and carbonyl values will be useful.

4. There was evidence, particularly in the oxidation studies, that much of the early polymerization in film formation involves reactions between conjugated double-bond systems and therefore probably results in direct carbon-to-carbon cross-linking. Other studies have indicated that cyclic products result from polymerization of such structures. By degradation techniques, the rings thus formed should be isolated and their structure determined. Studies of this sort have shown that polymerized eleostearates yield prehnitic acid, a ring compound with four carboxyl groups. Isolation and identification of cyclic arrangements and determination of the proportions of various cyclic types would establish the relative importance of carbon-to-carbon linkages and oxygen bridges in the oxidative polymerization of various unsaturated fatty acid esters.

5. A most important study could be made in the field of functionality. Since monofunctional molecules can form only dimers, and bifunctional ones only linear polymers, drying oils must contain at least some trifunctional molecules which can cross-link to form solid films. The properties of these films depend greatly on the proportion of zero, mono, bi, tri, and other polyfunctional molecules present in the mixture. As was stated in Chapter XIII, the average functionality of these molecules perhaps need not exceed two, and there may be distinct disadvantages if it does exceed two, in that unreacted unsaturated fatty acid radicals will remain in the hard film and undergo oxidative attack and degradation, thus causing undesired alterations in the properties of the film.

Therefore it appears desirable to prepare and study films from various mixtures in which the proportions of molecules with functionalities from zero to three are varied. For a start, simple mixtures of bi- and trifunctional molecules might be used.

The study should involve measurements of oxygen absorption, conjugated diene formation, setting time, hardness, adhesion, weathering properties, and indeed the whole gamut of properties included in this original Federation program.

6. As an extension of the investigation proposed in the foregoing section, further studies might be devoted to a consideration of the ideal proportions of saturated, oleic, linoleic, and linolenic acids that should be contained in an "ideal" drying oil. The present studies have demonstrated that no formulation is possible that will be ideal with respect to all desired properties. However, the relative proportions of the various acids (and alcohols) that would assure an ideal performance in individual properties might well warrant detailed study.

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